



**ALUMINIUM INDUSTRY  
AND THE ENVIRONMENT**

Seminar Papers and Documents



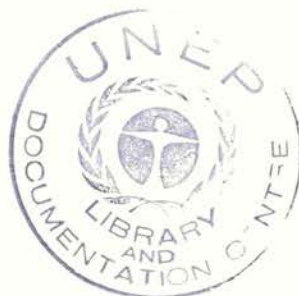
The General Assembly of the United Nations at its 27th session late in 1972 adopted Resolution 2997 (XXVII) declaring itself "Convinced of the need for prompt and effective implementation by Governments and the international community of measures designed to safeguard and enhance the environment for the benefit of present and future generations of man".

The Resolution stated further that the Assembly was "Aware of the urgent need for a permanent institutional arrangement within the United Nations system for the protection and improvement of the human environment", and proceeded to create:

1. A Governing Council for the Environment Programme composed of 58 member countries elected by the General Assembly.
2. A small secretariat to serve as a focal point for environmental action and coordination within the United Nations system to be headed by an Executive Director elected by the General Assembly on the nomination of the Secretary General.
3. An Environment Fund to provide additional financing for environmental programmes.
4. An Environment Coordination Board under the chairmanship of the Executive Director.

UNITED NATIONS ENVIRONMENT PROGRAMME  
Industry Sector Seminars

*ALUMINIUM MEETING*  
*Paris, 6th to 8th October, 1975*  
*Papers & Documents*



UNITED NATIONS  
ENVIRONMENT PROGRAMME



## FOREWORD

*From the first session of the UNEP Governing Council, held in June 1973, the importance of environmental issues associated with industrial development was recognized and a programme of activities on environmental problems of specific industries was initiated by the Executive Director.*

*A series of industrial sectors were chosen for examination by the Governing Council and the Aluminium Industry is one of these sectors. Consultations have been undertaken with experts nominated by Governments, industry and international governmental and non-governmental organizations, culminating in a Seminar held in Paris in October 1975, where the state of the art of existing remedies, outstanding problems and possible avenues of research and development to resolve these environmental issues were assessed.*

*This report gives the Proceedings of the Seminar, which includes the background papers prepared for the Seminar, as well as all the documents presented.*

*The views expressed in this report do not necessarily represent the decisions or the stated policy of the United Nations Environment Programme, nor does mention of trade names or commercial processes constitute endorsement.*

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Industry Sector Seminars

Aluminium Meeting

Paris, 6-8 October 1975

ANNOTATED AGENDA

1. Introductory Statements

- a) Mr. Maurice STRONG, Executive Director, United Nations Environment Programme, will outline the overall approach of his organization and the special concerns of the Industry Programme for abatement of nuisance, developments in low-waste and low-energy consuming processes, the impact on resources, and relations between Government and industry regarding environmental responsibilities.
- b) Mr. Ian MacGREGOR, Chairman of AMAX Inc., Greenwich, Connecticut, will deal with environmental issues as perceived by a chief executive officer of a major industrial enterprise.

2. Adoption of the Agenda

3. Purpose of the Seminar

A brief discussion of the purpose of the Seminar and its final output is envisaged. This item will be introduced by the Director of the UNEP Industry Programme. It is expected that the exchange of views between the representatives of Governments, international organizations and industry will make possible the selection of key linkages for information transfer. Inter alia, the Seminar may wish to consider :

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- Advising the Governing Council of UNEP <sup>(1)</sup>, through the Executive Director, on new mechanisms which should be developed by Governments, international organizations and industry for better utilization of experience and knowledge in environmental protection and resource conservation;
- Calling attention to priorities in relation to existing programmes and organizations;
- Identifying trends in future development of the industry of significance to the environment, especially those of importance to developing countries;
- Identifying, on the basis of experience gained in implementing statutory conditions in some countries, those aspects of regulatory control for protection of the environment which are now essential to maintain public confidence in any new installation, whether in a developed or a developing country;
- Producing a report incorporating the results of the Seminar which could serve as a useful guide to industry and Governments in dealing with the environmental issues.

As regards the eventual conclusions of the Seminar, discussion under this item should focus on the nature of such conclusions, and not on their context. As a working method, which has proven successful during the Pulp and Paper Seminar, it is proposed that a standing working group of rapporteurs be established, whose task would be to develop written conclusions to be agreed to at the final session of the Seminar.

#### 4. Discussion, for possible action, of general reports on the present situation

- 4.1. Paper I by Mr. W.D. RUCKELSHAUS on the present pattern of the aluminium industry and related environmental problems, and on possible future developments both economic and technological.
- 4.2. Paper II by Prof. M.C. FLEMINGS on resources and energy.
- 4.3. Paper III by Dr. I. NESTAAS on environmental impact and occupational health.

The function of the three papers is to provide a global picture through three different perspectives. Discussion at this stage is expected to be brief. (Additional papers may be received as background information for the Seminar).

#### 5. Examination of Specific Issues

- 5.1. Nuisances - with special reference to the containment of fluorides and hydrocarbons.
- 5.2. Problems of solid waste disposal - with special reference to the problem of

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(1) Conclusions and recommendations of this type would be the view of those present only, and would imply no commitment for their organizations or Governments.

bauxite residues arising from the production of aluminium.

- 5.3. Reduction of waste by recovery and recycling- with special reference to the difficulties of segregating and aggregating worthwhile quantities of aluminium metal from domestic waste and any other specific technical problems of purity in its re-use, for example, magnesium content.
- 5.4. Working environment - in the light of available knowledge in respect of protection in the industry, the progress achieved and research under way.
- 5.5. Lower energy techniques - with a view to indicating what work is in progress and the degree to which information could be available for exchange under commercial or governmental arrangements.
- 5.6. Availability of resources - in respect of suitable raw materials for the production of aluminium which will include the need for a high energy source and its environmental problems.

The discussion of each of the items above should be aimed at selecting the important issues for future co-operation. This should be considered in the light of whether international co-operation already exists, either within the industry itself or through international organizations, and whether there is a need to establish or strengthen co-operative links.

#### 6. New Prospects for Industry

This item will comprise a general discussion of the inter-relationships and mutual priorities disclosed in the detailed discussions under agenda item 5. Inter alia, the Seminar should consider the availability of natural resources and the effectiveness with which they are used in the complete system from mine to final application, including the capability to re-cycle. The possible effects that changes in production and utilisation practice may have on the fabrication of consumer goods should be borne in mind, with particular reference to value to be gained in respect of overall energy services.

#### 7. Output of the Seminar

In the context of the general structure, agreed under item 3, within which to present the findings and results of the Seminar, there will be written conclusions for examination on :

1. Identified possible trends in process developments, abatement techniques, immediate statutory provisions for installation and other measures intended to improve environment protection and resource conservation, and to minimize demands on energy.
2. Identification of the immediate statutory provisions considered important to establish good working relations between Government and industry in relation to operations of the aluminium industry, including major development agreements and guarantees, as well as more protective legislation.



3. Expression of opinion as to relative significance of different existing programmes of co-operation. Deficiencies in respect of international co-operation and suggestions, if necessary, for establishment of new mechanisms.

It is anticipated that the output of the Seminar will play a useful function in assisting the aluminium industry, Governments and international organizations in dealing with environmental problems.

8. Any Other Business

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**UNITED NATIONS  
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Mr. Maurice F. STRONG's OPENING REMARKS

UNEP's Aluminium Seminar

(Paris, 6-8 October 1975)

First of all, let me say that, although it is true, as my distinguished colleague, Mr. de ROSEN, has just remarked, that I have spent most of my life in the business field, those were the days when business was easy. As many of you, and even I, realise today, even this seminar is an illustration of the fact that today business is a great deal more complicated than it used to be. I do want to say, however, how pleased I am to join in the welcome extended to all of you by my distinguished colleague, Mr. de ROSEN, who himself brings to his assignment, as head of our Industry Programme, a very long record of successful business experience and, at the same time, devotion to public affairs.

I would like particularly to tell you how grateful I am for the interest manifested in our Industry Programme generally, in our task of creating a greater degree of rapport, understanding and hard cooperation between those in governments and in business who have the difficult task of reconciling environmental and social considerations with the demands of economic development and progress. I am pleased to see so many representatives of governments here, so many prominent representatives of industry and here I am delighted to have at my right a man, Mr. Ian Mac GREGOR who, as chairman of Amax, has himself long manifested a deep interest in, and concern for, the kind of issues we are discussing today. He is one of the people who first gave me the benefit of his guidance and support in these years when I undertook my responsibilities in the environment field and I am delighted that he is sitting here and he is at my right and is going to have a prominent role in the discussions of this morning.

I also like to thank the intergovernmental organisations who have sent their representatives to this meeting and who have helped considerably in preparing for it. Particularly, of course, I am pleased to see around this table some of my colleagues from the United Nations system itself. This, I think, illustrates both the degree of interest in the subject and the number of international organisations that are directly and intimately concerned with the subject matter of the seminar. I particularly want to pay tribute to the World Bank who have made available to us this very good, useful and congenial facilities and have done so in a spirit of real cooperation with a sister organisation of the international system. And I want to pay tribute too to the senior consultants who have contributed at the basic background papers on which this seminar will be based : Mr. RUCKELSHAUS, who certainly knows a great deal, probably more than any one in this room, about the difficult task of setting up fair and equitable regulations for an industry that is environmentally sensitive as the aluminium industry; his paper relieves me of the need to say many of the things that I might otherwise have said this morning ; Prof. FLEMINGS, Prof. NESTAAS who have both given us a very very significant detailed contribution which I hope will facilitate the deliberations of these next two days considerably. I also want to recognise the fact that it is Mr. de ROSEN's devotion to duty that has made the preparation, on UNEP side, possible.

I will not take long this morning but I would like, in these remarks, not to duplicate the comments made in the papers that you have received, rather more to outline briefly the general context in which this particular seminar takes place in relation to the overall concerns and activities of the United Nations Environment Programme. As you know, the U.N. Environment Programme was established by the General Assembly of the United Nations at its 1972 session in response to the recommendations of the Stockholm Conference which took place in June of that year. And its programme, the programme of the newly established UNEP was based very largely on the recommendations of that Conference. Some of you will recall that one of the principle feature of this Stockholm Conference was the broad recognition of the fact that the environment

issue went beyond pollution, that the environmental concern of some two thirds of the world's people was not centered solely around pollution but also had to take account of the very important range of environmental issues involved in the effective management of natural resource land, waters, plant and animal life in such a way as to get a maximum amount of development benefit from these resources without destroying the resource base itself. Therefore UNEP's programme has evolved in response to the needs and concerns of these two thirds of the world's people, two thirds of our constituency, as much as it has in response to the one third roughly of the world who live in the developed countries, where the environment issues first emerged very largely as a pollution issue. However, we recognised from the beginning that environment issues could not be treated as something simply added-in or added-on for very long. Of course, initially, the responses of environmentalists and of those who had responsibility in governments for administering environmental regulations, had necessarily to concentrate on what you might call the add-on or add-in approach, taking a look at plans for new activities from the point of view of whether they met certain environmental standards, taking a look at what needed to be added-on in terms of pollution control or emission control technologies or equipment to attempt to bring the pollution levels of existing industrial activities down to an acceptable level. However, I believe that your industry, the aluminium industry, is a very good example of the fact that we now need to look at these activities in an integrated manner. It is not only a matter of how to abate pollution but how to plan and structure the future development of the industry itself so as to minimise its overall environmental impact and ensure the basic objective of contributing to the growing needs for aluminium, the product of this case, within the limitations necessarily imposed by sound economics . This is not an easy problem but this, I am pleased to say, seems to be very much recognised by industry as the basic problem that faces industry in planning its future development and expansion and I am sure it is similarly the prime concern of those in governments who are called upon to establish and to enforce the regulatory climate within which industry must operate. It is not a

question of government versus industry or industry versus government , it is surely a matter of that common commitment to the need for expanded economic progress but an economic progress which contributes to the real growth and development of society in terms of social as well as economic objectives without inflicting unnecessarily damage on the health, on the land, on the aesthetic qualities of the environment. Here there can be no absolute; there can not be absolute commitment to economic goals which defy any considerations of environmental and social interest nor can there be any unmitigated commitment to environmental and social goals which do not take into account the need for the industry to contribute its important part to the need for economic growth. Now our Industry Programme is based upon the fact that, in respect of many industries, and it is certainly true of the aluminium industry, there is a very important international dimension and that the conditions which are encountered in one country affect its investment programmes not only in that country but in other countries too. Equally, governments, for a large part, are themselves faced with the need to respond to the fact that what other governments do in respect of their industry, affects their freedom of action, in terms of the competitive position of their own particular industry. Therefore, we have tried, from the inception, to base our approach on the need for a greater sharing of basic background data, of information, of concerns, on the basis that it is by a more sophisticated common information base that both governments and industry can do their respective jobs of trying to assure that the environment is protected, whilst the commitments to economic growth are equally protected. It is a proper balance between these two factors. We are doing this not by prescribing any general cures; we recognise, of course, that the situation of each country is different, its goals are different, its particular environmental circumstances are different, its priorities are different, its need for economic growth in the aluminium sector is different, its basic raw material situation and its labour situation are different, so there can be no general prescription of specific remedies; however, the fact that both industry and governments work from

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a common base of data, a common understanding of each other particular problems will, in our view, assure that industries, as they confront government regulators around the world, will have a better understanding of their problems just as those who establish and regulate environmental and growth development policies in the framework of governments will have a better understanding of industry problems and concerns and realities.

This means that we do not aspire to setting absolute standards. However, we do want to go as far as possible in establishing guides that are useful both to industry and governments, guides which point up the areas where there seems to be a rather common acceptance of a certain set of factors, guides which point up differences too, important differences or unresolved areas where we all recognise, of course, that science has not provided us with perfect answers to some of our problems, that there may be different views, quite legitimately based on incomplete scientific evaluation of some environmental problems, particularly health effects. There are many areas where science has not yet given us final answers and where there is legitimate a cause for concern. Industries need to realise that governments have a greater concern in areas which directly affect human health, concern which may result in their wanting to give human health the benefit of the doubt in any regulations which they establish, while industry, of course, properly has the goal of economic growth as its principal responsibility. So there is a logical and necessary tension between the two roles. So we should not feel that all conflict is bad. I think that it is to create a better framework for the constructive identification and resolution of conflict and tension between these two necessarily different points of view, two necessarily different sets of responsibilities, that our Industry Programme has been established.

May I also say that, and some of you know it, we have, in addition to our Industry Programme here and as a complement to it, the benefit in Nairobi of the Centre for Industry and Environment which has facilitated very much our communication with industry, our ability to identify common areas where we should be informing

each other more closely. I want to commend those who have supported the establishment of this Centre. It is doing a very useful job as a complement and supplement to our programme.

That brings me to another point where I would like to say that we, in UNEP, do not feel that there is any part of our programme which can simply be closed in a category and which can then make us feel, or make industry feel, that we have looked after the participation of, or the interest of, industry. Although we have an Industry Programme, Mr. de ROSEN is the most vocal spokesman, and I support him completely on his concept that industry has an interest in our total programme. For example, one of our priorities, one of our major priorities, is the pollution of oceans. A Law of Sea Conference has been attempting to resolve some of the global concerns that are needed to be dealt with before agreements on the establishment of a seabeds and oceans regime are reached. We have been working in cooperation with this group but, at the same time, we have been working on the whole question of the regional seas. The Mediterranean is perhaps the best example of the importance of this area of our activities to industry. The Mediterranean is one of the oldest seas, one of the most in danger in environmental terms; around its fringes, much of the civilised life of the western world was originated and many of the adverse consequences have also become most evident. The comprehensive plan that has now been agreed in principle by governments, as a result of the meeting in Barcelona and which shortly should be confirmed in a formal convention and protocols will call for a comprehensive programme not only on a pollution control of the sea, but also for control of industrial and urban activities on the main land of the Mediterranean countries. This is going to have very significant implications for the industry of that area. I could further cite the Caribbean and various other seas which are on our agenda too, regional seas where the role of industry is going to be extremely important.

The establishment of a new International Register of Potential Toxic Chemicals is another area of activities that are proceeding. We will soon have a centre established, probably in Europe, the first ever, which will be an international register of potentially

toxic chemicals and which will permit identification of risk and of sources. This, too, involves a very important industry.

We have about ten major priority areas; one is the Global Environmental Monitoring System; another International Referral Service which is a global information service designed to support governments decision-making in the environmental field by assuring that they have access to the best experience, the best technologies available. This, too, is important for industry.

I think I have said enough to make my case for the fact that industry is interested and is affected by virtually all of our programme activities and there are probably few of the more than 300 specific UNEP projects, that have now been launched in every part of the world, that do not, in some fashion, bear upon the interests of industry. In fact, many of them depend upon the active cooperation and response of industry. Industry is a source of technology. It is a source of management and it is only by changes that occur within industry itself that many environmental problems can be fully addressed.

Finally let me say that it is my belief that the whole environment issue is moving out of the add-on and add-in stage where you sort of take an extra look at particular projects from the environmental point of view, to the very centre of the whole growth area. It is being recognised that many environmental and indeed related social concerns can only be dealt with by a more comprehensive integrated approach to growth and development itself. And environment has to figure very much in the whole planning and development stage of industry programmes. This is why I think your industry, the aluminium industry, is a particularly good example because, as the papers point out, you have many pluses and minuses that make believe that the industry is a big pollutant in some areas, whilst it is difficult to change significantly the many existing plants and expensive to have them achieve desirable pollution control levels. On the other hand, you are big energy consumer. But the product



itself brings many special, indeed unique, qualities into the environmental scene or what you might call the era of environmentally related growth: many positive features, which no other competitive metal can match, compounded with the progress made in reducing the energy required to produce a unit of aluminium production. I am delighted at the potential for recycling and recovery of waste that is inherent in your industry and which is already being exploited to some extent. The potential use of aluminium in such other energy alternatives as solar energy which is pointed out in the reports prepared for the seminar is, I believe, another example of the degree to which your industry can play a very environmentally positive role. And I would like to suggest to you that if this seminar, in the next two days, can produce as much of a range of agreement or consensus as is possible on specific issues, as much consensus as possible on those issues in which more work must be done, more scientific work, more work by industry, more work by governments, where important differences or conflicts can be identified, this will be a very important result. It will be conform to our desire to assure that these industry seminars help to bridge the gaps that exist between governments and industry and will create a more harmonious climate for industry expansion in ways which will be compatible with environmental goals. It is not a question of how to keep the industry down, it is a matter of how to permit it to grow under environmentally compatible conditions.

Most of all, beyond the specific results that you may produce, I hope this will be the beginning of a spirit of cooperation that will benefit both industry and governments. There are important developing countries whose importance in aluminium industry is pointed out in your papers. They are not here and one of the reasons is that many of them do not have the people yet skilled to respond to the kind of professional dialogue we are having. One of our jobs, I remind you again, is to serve the two thirds of the countries in the world which are developing countries. Much of the aluminium industry future is related to expansion in the developing world. We must see the whole environment for the industry in the context of the aspirations and the interests and the concerns of the developing countries as reflected in their drive for a new international

economic order. These cannot be shelved under the table or ignored by industry. These are important political questions that are at the top of the agenda of the countries on whom the future of much of your industry depends. These concerns must be shared and understood by industry people because they do prepare the broad contacts on which the future of much of your industry does depend. Therefore, we feel a special role on behalf of those not here today. They will be seeking our guidance. We will be making the results of this seminar available and we will be giving them technical assistance in helping them to frame their regulations and legislations in respect of your industry. Despite the fact that they may not be here in person, you fell responsible for them just as we will see to it that the results of this seminar will be brought to their attention so that they may frame their response in the growth plans and needs of your industry.

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6 October 1975



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Aluminium Meeting

Paris, 6-8 October 1975

INTRODUCTORY PAPER

Prepared for UNEP

by

William D. RUCKELSHAUS ( U.S.A. )

As one who has administered a program of environmental regulation, I particularly welcome this series of industrial seminars on environmental problems as a vital step in achieving and maintaining international environmental quality. For the significance of this meeting ranges far beyond the narrow concerns of aluminum production and usage. This seminar, like its predecessor which dealt with the pulp and paper industry, and the subsequent sessions which will deal with the petroleum, motor vehicle, iron and steel, chemical and other industries, signals a growing candor among concerned nations about our common environmental difficulties and an encouraging willingness to think through our problems to mutually beneficial solutions.

I have been concerned since the United Nation's Conference on the Human Environment in Stockholm in 1972 that the emerging concern for environmental issues neither be misrepresented nor misunderstood. Environmental consciousness is not and cannot be a luxury only the industrialized nations can afford. For

the industrial nations have learned from bitter experience that their advancing prosperity in the twentieth century is a mixed blessing, which if not managed wisely could threaten bankruptcy in the twenty-first century. Increasingly we have begun to realize that environmental problems are problems of resource management -- management of the vital resources (air and water) necessary to the sustenance of life; management of the land resources upon which we depend for the cultivation of our food and the settlement of our people; management of the mineral resources deposited in the earth and which we can fashion into instruments for the enhancement of human life.

The simplistic and often too popular conception of environmental quality as a matter of pristine conservation is a fallacious one. Clearly the resources of this planet should be used for man's benefit. The challenge to mankind in the last quarter of this century, however, is not to continue a headlong rush into a counterfeit prosperity, but rather to plan and achieve an enduring prosperity that all nations can share. That challenge is one of sensible and efficient resource management.

Thus, the significance of this seminar and its counterparts. The sharing of attitudes, approaches, problems and solutions we attempt here does not seek a competitive advantage or disadvantage for any nation or group of nations. Our attempt is to share experience and insights that will help us all achieve efficient

resource management, enduring prosperity, and a life-sustaining and enhancing environment.

It is especially fitting that we gather in this international setting, under the auspices of the United Nations, to consider the problems of the aluminum industry. For the aluminum industry is international by its very nature. In large measure the aluminum industry is conducted by multinational corporations, and the total number of countries producing primary aluminum throughout the world rose in 1973 to 38. With the exception of the Arctic poles, aluminum is produced on every continent of the globe. From the extraction of the basic source material at bauxite sites (and similar ore sites) located in a number of countries around the world, to its fabrication and distribution in every nation on earth, the aluminum industry should be viewed with a world-wide perspective.

The basic electrochemical process by which aluminum is produced has remained essentially unchanged since it was first discovered simultaneously by Charles Martin Hall and Paul L. T. Heroult in the latter part of the last century. Aluminum production results from the electrolytic reduction of alumina. Alumina, an intermediate product, is generally produced from bauxite, a naturally occurring ore of hydrated oxides of aluminum. The major world sources of this essential bauxite ore are South America, the Caribbean, and Australia.

In general terms, the production process is thus: alumina is shipped to the primary reduction plant where it is electrically reduced to aluminum and oxygen. This reduction process is carried out in shallow rectangular cells (pots) made of carbon-lined steel with consumable carbon blocks which are suspended above and extend down into the cell. The cells and carbon blocks are connected electrically to serve as cathodes and anodes, respectively, for the electrolytic process. Cryolite, a double fluoride salt of sodium and aluminum, serves as both an electrolyte and a solvent for alumina. Alumina is added to and dissolves in the molten cryolite. The cells are heated and operated between 950 and 1000 degrees centigrade with heat generated by the electrical resistance between the electrodes. During the reduction process, aluminum ions migrate to the cathode where they are reduced to aluminum. Because it is heavier weight, the aluminum remains as a molten metal layer underneath the cryolite. Oxygen ions migrate to and react with carbon in the anode to form carbon dioxide and carbon monoxide which continually evolve from the cell.

Alumina and cryolite are periodically added to the cell to replenish material which is removed or consumed during normal operation. Periodically the molten aluminum is siphoned or "tapped" from beneath the cryolite bath and moved to holding furnaces where the product aluminum is held in the molten state

until it is cast into ingots or billets to await further processing.

Because of discrepancies in energy requirements and emissions control, it is important to recognize that basically three different types of cells are used for the production of aluminum: the vertical stud Soderberg, the horizontal stud Soderberg, and the prebake. For the purposes of this paper one only must note that the primary difference among these cells is their physical configuration in terms of the provisions for introducing the electrical current across the cryolite bath. Although they require more power, the Soderberg systems were initially utilized on a wider basis because they did not require a separate facility to manufacture anodes. Soderberg cells permit the consumable anode to be baked in situ. A mixture of ground coke and coal tar pitch is periodically added to the top of the electrode where heat from the process drives off the lower boiling organics and fuses the new material to the old electrode. In contrast, the prebake cell uses an anode that is precast in a separate facility. Since the anode is consumed during normal operation, old anode remnants must periodically be replaced with new anodes.

In the case of the Soderberg systems, however, partially because of the problems with the volatile pitch which condenses in the duct work and the control device, and partially because of the problems inherent in simultaneously



controlling fluorides and organic emissions, as well as the rising costs of energy, any previous economic advantage of the Soderberg systems is diminishing and the trend at least in the industrialized world is toward utilization of the prebake cell.

Whatever system is utilized, however, the end product is a lightweight metal possessing many valuable characteristics: durability and strength, electrical conductivity, the ability to reflect or conduct heat, and an attractive surface. For these reasons steadily increasing applications of aluminum in the construction, transportation, packaging, and electrical industries, as well as in the manufacture of machinery and consumer goods, have been made over the years.

In the decade 1963 to 1973 world production of primary aluminum increased at an annual rate of 8.5 percent. During this decade world primary aluminum production more than doubled from 5,862 thousand tons to 13,286 thousand tons, an increase of over 127 percent. It is important to note that this increase in production occurred on a truly worldwide basis.

The greatest percent increase during this period was in South America which experienced a ten-fold boost in production. Oceania (Australia, New Zealand) experienced a four-fold rise in production. Asian production more than quadrupled in this period, moving from 431 thousand tons in 1963 to 1,771 thousand tons in 1973. In this same period North American and European production increased 85 and 124 percent respectively.

To achieve sound and efficient resource management requires the assessment of many factors. Unquestionably by the extraction of alumina from the natural ores and by the subsequent reduction of alumina into aluminum, man has created an important and beneficial new resource. He has done so, however, at costs beyond those required in capital and labor expenditures to produce an ingot of aluminum. These non-capital costs must be recognized and the trade-offs established in order to make sensible determinations of efficient resource management.

The production of aluminum, like the production of any resource, by its very nature entails the production of unwanted by-products which can have a deleterious effect on both the general environment and the work environment. The ability to control these unwanted by-products is an important factor in assessing resource management.

The first unwanted by-product resulting from the production of aluminum is the residue from extracting alumina from bauxite. By volume, only 50 percent of the bauxite mined and processed is turned into alumina. What remains is a red-brown muddish residue that must be disposed of somehow, either by discharge into waterways or impoundment upon land. In my own country the practice has been largely impoundment upon land, but in geographical areas where the rainfall can exceed the rate of evaporation of this wet material, sand beds must be prepared to impound the residue.

In the reduction of alumina to aluminum, both particulate and gas emissions occur which have a detrimental effect on air quality. The emission of hydrocarbons, sulfur dioxide, carbon monoxide, and fluorides from aluminum production plants can be controlled, however, by the application of either dry or wet air pollution control systems to production facilities. With the utilization of both primary and secondary control systems, including wet electrostatic precipitators, 90 to 95 percent of the impurities can be collected and prevented from discharge into the atmosphere.

To control these emissions obviously entails considerable cost, and thus increased production costs for aluminum. It is especially expensive to retrofit control systems to existing plants where the operational life of the plant may nearly be exhausted. Fluorides are one of the most costly emissions to control and also the most controversial in terms of the hazard it represents.

The deleterious effects of fluoride on both animals and vegetation have been extensively documented. The effect on animals occurs through the digestive tract when relatively large quantities of contaminated vegetation are ingested. But present evidence indicates that fluorides in the range of ambient concentrations encountered under the worst conditions do not damage human health through inhalation, except in industrial exposure. In the United States we have adopted a course of fluoride regulation because we have concluded that

fluoride emissions adversely affect public welfare not only through their effects on aesthetic values, but also through a decrease in the economic value of crops which are damaged by exposure to fluorides and through adverse effects on the health of animals ingesting vegetation which has accumulated excessive amounts of fluorides.

The production of aluminum also involves of necessity certain hazards in the work environment. Due to the temperatures at which the cells must be heated for the electrolytic reduction of aluminum to occur, heat stress is a very real health hazard requiring the provision of cool-out rooms in which workers can take respite from the high temperatures. Moreover, the coal tar pitch volatiles present in the industrial process result in particulate polycyclical organic matter which it is unhealthy to breathe. A possible solution to this difficulty is to require workers to wear respirators when working in the cell. The tremendous heat of the cell, however, renders the weight of the respirator a significant burden for the worker and a potential health hazard itself. In my own country we are currently in the process of trying to determine a proper health standard for this problem. Finally, fluorine, as noted earlier, can be hazardous to human health when directly inhaled in heavy concentrations, as in industrial exposure.

Two very significant and interrelated factors bearing on an assessment of the efficient resource management of aluminum remain: the energy requirement to produce aluminum and the recyclability of the metal.

Historically the production of aluminum has been an energy intensive enterprise. Prior to the Second World War it required 12 kilowatt hours of energy to produce a pound of primary aluminum. Technological advances in the post-war world enabled producers to reduce energy use to 10 kilowatt hours per pound of primary aluminum. Today the aluminum industry is operating with a requirement of 8 kwh per pound of primary aluminum, but the technology has already been developed to construct a greenfield plant that would require 6.5 kwh per pound.

Beyond these reductions in energy use even further reductions are being tested and researched. Pilot plants are being developed which, if proven commercially successful, could have far-reaching energy and environmental consequences in the aluminum industry. For example, Alcoa has developed a new electrolytic method of producing primary aluminum which is expected to reduce by as much as 30 percent the electricity required by the most efficient units of the Hall process presently used world wide. As well, the new process uses a system which is expected to be free of undesirable emissions and provide a superior working environment.

In addition to requiring less energy, the Alcoa Smelting Process is expected to be more tolerant of power interruptions than is the Hall process and could accept power reductions during daily periods of peak demand by the public. Its total operating costs are expected to be lower, and it is designed so that it would permit plants to be located on smaller sites with greater location flexibility. This new process has been tested in a development unit and will now be evaluated in a full-scale pilot plant.

In this new process alumina is combined with chlorine in a reactor unit which chemically converts the oxide to aluminum chloride. The chloride is then electrolytically processed in a completely enclosed cell which separates the compound into molten aluminum and chlorine. The chlorine is continuously recycled back to the reactor in a closed loop which obviates the need and cost of containing emissions.

Beyond the development of the Alcoa Smelting Process research is underway in several companies to test a chemical aluminum-producing method as well as to develop bauxite substitutes by making alumina from anorthosite, alunite, laterite and clays.

Thus advancing technology has played a significant role in the steady reduction of the energy requirement for aluminum production, and it appears it will continue to do so. The energy factor, however, must be viewed in light of the most hopeful

characteristic of aluminum -- its recyclability. Aluminum is eminently recyclable for a number of reasons, but especially because of its high scrap value which is substantially higher than most competitive materials. The extent to which the aluminum industry has the potential to recycle means savings in energy, raw materials and capital investment far beyond what is now possible in competing industries.

The energy savings are particularly dramatic. Every pound of aluminum recycled to ingot conserves 95 percent of the energy required to produce primary aluminum. Moreover, since aluminum can be recycled repeatedly, as the consumption of aluminum rises the availability of aluminum for recycling rises.

For the four year period 1973 through 1977, the United States aluminum industry set itself a goal of increasing the industry's annual metal supply by one billion pounds through recycling. That is an ambitious goal, but the metal is there to achieve it. It is estimated that some three billion pounds of scrap aluminum are lost in the solid waste stream each year in our country. An additional one billion pounds of aluminum recycled would save mining and importing about two-and-one-half million tons of bauxite; at least 6.5 billion kilowatt hours of electrical energy; and, at current costs, it would save a capital investment of at least one billion dollars.

It is important to achieve this goal, I think, because of the opportunities for economical re-use as minimal energy costs keep expanding. This is particularly true of products which have a rapid distribution cycle. A good example is the aluminum can. Conceivably the metal in a single can could be recycled and reused three or four times in a given year. Last year in the United States the equivalent of 2.3 billion aluminum cans, or 17 percent of those used during the year, were recycled. Though still only a fraction of the total, this represents a significant increase over past performance. Obviously automotive scrap has a much longer recovery cycle, but the amount of aluminum in cars as well as the number of cars becoming obsolete is increasing. As the trend to more aluminum in cars intensifies, substantial additional sources of scrap will become economically available.

Another important aspect of the recyclability of aluminum is that it reduces the problem of solid wastes. Waste and scrap are generated at various stages during the production of primary aluminum, mill and foundry products, and during the manufacture of finished industrial and consumer products. It is estimated that for every ton of aluminum processed into finished products more than a quarter of a ton of scrap is generated.



Primary aluminum producers, aluminum foundries, and aluminum fabricators recycle the waste and scrap they generate, and in some cases they also recycle scrap they purchase or receive from others. Manufacturers of industrial or consumer products usually dispose of their aluminum scrap to scrap dealers, secondary smelters or aluminum suppliers. Secondary smelters purchase scrap for the manufacture of secondary aluminum which is sold primarily to aluminum foundries.

Of course, post-consumer recycling of aluminum products reduces the amount of solid waste that must be disposed of. Recycled aluminum cans are being made into raw metal rather than causing a disposal problem. Projected greater use of aluminum in automobiles should help the junk car problem by enhancing the scrap value of the car. Because of its high scrap value, aluminum also will play a major role in making municipal refuse recycling plants economically feasible.

Along with technological advances and recyclability, two other elements bear directly on an assessment of the energy factor in aluminum resource management. One is the durability of the metal. For example, two given products may require the same amount of energy to manufacture, but if one has three times the life span of the other, its energy content is reduced by two-thirds. The other element is that aluminum is a relatively lightweight metal, thus affecting substantial savings in the energy costs of shipping products. For example, twice as much beverage per gallon of gasoline can be shipped in aluminum cans as in refillable glass bottles. Indeed energy savings are possible in many areas of the transportation industry through the utilization of aluminum which would reduce vehicle weight and thus boost gasoline mileage. (A further discussion of this point occurs later in this paper.)

The worldwide recession and economic dislocation of the last few years have had a pronounced affect on the aluminum industry. Rising fuel costs throughout most of the world and the

cartel formed by the bauxite producing nations to raise the price of the raw material have driven costs upward while lagging consumer demand has resulted in the industry operating at reduced capacity. While primary aluminum capacity is expected to grow in the immediate years ahead, it surely will not grow at the rates experienced in the decade 1963-1973. A sizeable proportion of the growth which does occur in the near-term future is likely to occur outside the industrial nations for several reasons:

As mentioned earlier, the bauxite countries are attempting to place a new value on their resources. Not only have they formed a cartel to raise the price, but they are moving toward alumina and aluminum production and that trend is likely to continue. Aside from some bauxite deposits in Europe, the known sources of bauxite are: Jamaica, Haiti, Costa Rica, Surinam, Guyana, French Guiana, Brazil, Ghana, Guinea, Sierra Leone, Cameroon and Sumatra, Java and Borneo in Indonesia.

Moreover, despite technological advances the energy requirements for the production of aluminum are still considerable, especially in an environment of rising fuel costs. One approach to this problem is to locate stable sources of hydroelectric power for the production of aluminum. An aluminum industry survey of potential hydroelectric power sources for the production of aluminum reveals that outside of Norway and Iceland these sources are located in the non-industrialized nations: Colombia, Venezuela, Brazil, Guinea and Zaire.

The advantage of the lower cost power countries also makes the Middle Eastern countries a potential source of new aluminum production. Worldwide the aluminum industry is experiencing a capital shortage, but the influx of petro-dollars and other currencies into the Near and Middle East provide a capital accumulation to combine with abundant oil and natural gas resources for the production of aluminum. At this time a number of Near and Middle East countries are debating the erection of new or additional primary aluminum capacity, including: Iran, Iraq, Kuwait, Saudi Arabia, Qatar, Abu Dhabi and Algeria. The total smelter capacities being considered is 1,400,000 metric tons annually, which would raise the combined capacity of the Middle and Near East to 1.8 million tons per year, a very sizeable proportion of the world total.

Beyond the near term, the prospect for aluminum production and consumption on a long term basis is steady expansion. The innovative application of aluminum to vital areas of human needs will continue. Four areas especially hold great potential for greater utilization of aluminum: transportation, shelter, energy transmission, and food packaging and distribution.

In terms of transportation, aluminum's light weight and strength, corrosion resistance and formability give it an important role in products that are designed to move, particularly the automobile. Increased use of aluminum can greatly reduce

the weight of a car and thereby increase mileage per gallon of gasoline. Experience has shown that a single pound of aluminum used in an auto part produces an immediate and direct weight saving of one and one-half pounds when substituted for traditional materials. Consequently, this saves another three quarters of a pound by allowing lighter structural supports.

In the United States in 1974, with an average of about eighty pounds of aluminum per automobile, it is estimated that somewhere between 1.6 to 2.5 billion gallons of gasoline was conserved. If aluminum substitution were increased to 420 pounds per automobile, a weight reduction 30 percent below 1974 figures could be achieved with consequent fuel savings as a result.

Automobile makers around the world are accelerating the basic redesign of automobiles to reduce weight and conserve fuel. Aluminum will be an important factor in this redesign. This should be true as well for trucks, farm and industrial vehicles of all types, and railroad, marine and mass transit applications. The reasoning is simple; aluminum truck or vehicle bodies can deliver more product per transportation energy unit expended than heavier wood or steel products.

Rising energy costs should also prove a stimulus to greater utilization of aluminum in building and construction, where aluminum has the potential of making buildings of all kinds more durable and more energy efficient. The proper combination of aluminum building products have been proven to reduce heating, air conditioning and maintenance costs of buildings.

If the predictions of some experts that solar energy will come into widespread use in the next decade come true, the heating and cooling of homes and other buildings by solar energy will create a vast new market for aluminum. A 500 square foot solar collector panel, the size which it is estimated will be required for an average home, contains about 750 pounds of aluminum. In my own country the Congress has authorized more than a billion dollars in Federal funds over the next four years to encourage the development and use of solar energy.

In the field of energy transmission aluminum is a critical element because it is the most economical conductor of electricity. In the United States more than 90 percent of the overhead transmission lines are aluminum. It seems clear that in the future, one way or another, the world will be increasing its energy sources and supplies. This will entail additional transmission and transportation equipment, much of which is likely to be made of aluminum.

Packaging -- especially the packaging and distribution of food -- also holds out potential for increased demand for aluminum. From storage silos to large shipping containers,

from beverage cans to meat and vegetable packages, it is expected aluminum will increasingly be used to help protect and distribute our food staples.

In the United States we have pioneered the growth of the aluminum beverage container. The can is now beginning to gain popularity in Europe, Japan, Australia and other parts of the world. The unique energy and environmental advantages of the recyclability of the can should lead to increased worldwide usage.

Another application of aluminum of even greater potential is the retortable aluminum pouch which is designed as a replacement for the traditional tin can for the packaging of perishable foods. In Japan and here in Europe this new package is now being tested and hailed by many as the food package of the future.

From just these four primary areas -- transportation, shelter, energy transmission and packaging -- I believe it is apparent that there will be a continuing rise in demand for aluminum. Some of this demand will stem in large measure from the need to substitute aluminum for other materials where light weight or durability are essential to conserve energy. Some of the rise in demand will result when one or more of aluminum's other properties provide net energy efficiency and economy. In some cases it may rise from our need to stretch the world's supply of scarcer materials by substitution with aluminum.

Because it is the most abundant metal in the earth's crust and because its versatility permits its use as a replacement for many other basic materials in many applications, the prospect for expanding aluminum production and usage is nearly a sure one. More importantly, the potential for clean and efficient resource management of aluminum is great because of its recyclability, technological advances in reducing the energy requirements to produce the metal and the possibility looming on the horizon of producing aluminum in a closed loop system that prevents the generation of harmful emissions.

One fact is certain. The additional aluminum capacity that will be created world wide in the years to come can -- with sound planning -- be constructed to minimize the environmental hazards the industry has known in the past. Hopefully, one of the consequences of this seminar will be that we can learn from our mistakes and the mistakes of others. In the long run it is cheaper as well as better to anticipate the environmental consequences of our actions and undertake to control them than it is to proceed with abandon and then attempt to reclaim what has been squandered.





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A SURVEY OF POLLUTION PROBLEMS  
IN THE ALUMINIUM INDUSTRY

Prepared for UNEP  
by  
Ivar NESTAAS (Norway)

## A B S T R A C T

This paper contains a general survey of the environmental problems of the aluminium industry, covering the steps from bauxite mining to processing of scrap.

The main emphasis is placed upon air pollution caused by generation of fluorine compounds during production of primary aluminium by electrolysis. Emission data for various types of pots and gas cleaning plants and the nature of effects on the environment are reviewed. Other environmental problems of the electrolysis plant include water pollution, solid waste disposal, working conditions and auxiliary operations. These topics are covered in general terms.

Environmental aspects of bauxite mining, alumina production, manufacturing of aluminium goods and processing of scrap are discussed briefly.

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## 1. INTRODUCTION.

### 1.1. Scope.

The purpose of this paper is to give a general outline of the environmental problems of the aluminium industry, covering the steps from bauxite mining to disposal or recycling of goods made from aluminium.

Air pollution problems of electrolysis plants are generally considered the most important environmental problem of the aluminium industry, and the paper pays special attention to this topic.

### 1.2. A Brief Outline of Environmental Problems and Related Production Technology.

Figure 1 shows a simplified diagram of the main processes of the aluminium industry and related pollution problems.

Bauxite is extracted by open mining and converted to aluminium oxide by chemical processing. The process creates large quantities of solid waste. Production of aluminium takes place by electrolysis of aluminium oxide dissolved in a smelt containing fluorine compounds. Some fluorine compounds escape from this process, creating an air pollution problem. Herbivores and several types of plants are especially vulnerable to these compounds, and many aluminium smelters have for

this reason installed air pollution control equipment. Molten metal is transferred to the foundry, normally on site of electrolysis plant, for adjustment of composition and casting to ingots and other products. Manufacturing of finished goods takes place by a number of processes, such as rolling, extrusion and casting. Major applications of aluminium are in packaging, building materials, electric installations and transportation. Most aluminium scrap generated during manufacturing is recycled, but a large percentage of discarded packaging and other small items are wasted.

## 2. BAUXITE MINING AND REFINING OF ALUMINIUM OXIDE.

### 2.1. Mining.

Aluminium oxide is made from bauxite, composed mainly of oxides of aluminium, iron and silicon. Other minerals are used to a limited extent, but may become more important. Globally, minerals containing aluminium are plentiful.

The largest deposits of bauxite are in tropical areas, far from major metal producing countries. Bauxite is generally extracted by strip mining, blasting or earth-moving equipment is used according to the state of the bauxite. Strip mining normally has a major negative effect on the local environment. Extensive precautions are required to re-establish satisfactory topography, ground conditions and vegetations. Some mines scrub their bauxite to remove silicates, thus producing large volumes of water containing suspended solids which have to be removed to avoid water pollution.

## 2.2 Production of Aluminium Oxide.

Processing of bauxite to aluminium oxide generally takes place at plants located independently of the smelters. The major quantity of oxide is manufactured by the Bayer process. Main steps of this process are extraction at high temperature with a solution of sodium hydroxide to form sodium aluminate, followed by precipitation of alumina hydrate and calcination to remove water.

Heat requirements of the process are considerable, causing emissions of sulphur dioxide from fossile fuels. Calcining and handling of materials may cause dust problems, electrostatic precipitators and other types of equipment are required to reduce these emissions.

Large amounts of "red mud", a fine precipitate containing compounds of sodium, iron, silicon and aluminium, are a waste from the Bayer process. The quantity may, depending on the composition of the bauxite, be 0.5 - 1 tons, dry weight, per ton aluminium oxide. The mud normally contains 20-30% of solids, this may be increased to 40-60% by filtration. The accompanying water is highly alkaline and contains some aluminium and sodium. Most of the "red mud" is currently disposed of in ponds or by landfilling or in the sea, by dumping or submarine pipelines. There is a growing concern about the environmental effects of these methods. The present trend in industrialized countries seems to be towards prohibiting dumping at sea and

demanding extensive precautions at landfilling sites to reduce land requirement and prevent leaching of pollutants. One satisfactory method of disposal consists of landfilling of filtered mud, the site being arranged for recovering alkaline leachate to be returned to the process. The top of the fill is then covered with soil. A number of processes for utilization of the "red mud" have been studied.

By one alternative to the Bayer process, the Pedersen process, bauxite or other raw material is converted to aluminium oxide pig iron and slag by electric smelting followed by chemical processing. As the slag can be used as a raw material for cement, total utilization of the raw materials may be achieved. High energy consumption is a disadvantage of the process.

### 3. PRIMARY ALUMINIUM PRODUCTION.

#### 3.1. Electrolytic Reduction.

##### 3.1.1. Production Technology.

Aluminium is at present produced by the Hall-Heroult electrolytic process exclusively. Two alternative processes, one based on electrolysis of aluminium chloride and the other on reduction of aluminium oxide by manganese, may however become alternatives in some years. An experimental, industrial scale plant using the chloride process is expected to be in production in USA in 1975. This process used no fluorine compounds, and is said to be 30% less energy consuming than the Hall-Heroult process.

Aluminium is produced by electrolysis of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) dissolved in a melt consisting mainly of cryolite ( $\text{Na}_3\text{AlF}_6$ ), a compound which contains fluorine (F), at about 960 - 980°C. Typically, the production of one ton of aluminium requires 1.9 tons of alumina and consumes 0.5 tons of carbon anodes, 35 kg of fluorine and 17.000 kWh of electricity. There are however considerable differences between individual production plants, or smelters. Fluorine is added mainly as aluminium fluoride ( $\text{AlF}_3$ ) to replace losses caused by evaporation, splashing and absorption in the pot lining.

The electrolysis is carried out continuously between carbon electrodes in pots lined with carbon and insulated with bricks. Examples of pot designs are shown in Figure 2. Pots are classified



as prebake (PB) or Søderberg (S) pots according to design of the anode. Most prebake pots have anodes consisting of carbon blocks which are replaced after partial consumption. Søderberg pots have continuously operating anodes which are baked on the cell. Søderberg pots were previously designed with horizontal electrical contacts (HSS pots), while vertical contacts (VSS pots) have dominated in plants built during the two last decades.

Smelter capacities range from about 10.000 to 400.000 tons annual capacity. A smelter may have one or more pot-lines, consisting of pots electrically inter-connected in series. A typical pot-line of 50.000 tons installed capacity may have 220 pots of 100 kA each. The pots could then be arranged in two parallel lines and placed in two pot-rooms, each being about 500 m long and 30 m wide. Figure 3 shows an example of pot-room design.

### 3.1.2. Air Pollution - Still the Main Environmental Problem.

#### Formation of Air Pollutants.

Figure 4 shows the structure of the fluoride problem of the Hall-Heroult process. It also shows the main influencing factors which may provide opportunities to solve the problem.

Air-borne fluorine compounds, generated in the pots during electrolysis, vary considerably in quantity and composition. Typical rates of generation are about 20 kg F per ton of aluminium from

Söderberg pots and about 16 - 22 kg F from PB pots with side and central crust-breaking, respectively. An appreciable percentage of these emissions is HF. There are even small amounts of carbon-tetrafluoride ( $\text{CF}_4$ ). The rest is in solid state, mainly as cryolite ( $\text{Na}_3\text{AlF}_6$ ) and chiolite ( $\text{Na}_5\text{Al}_3\text{F}_{14}$ ).

The sulphur content of the carbon anodes is released as sulphur dioxide ( $\text{SO}_2$ ). Furthermore, considerable quantities of carbon monoxide (CO) and carbon dioxide ( $\text{CO}_2$ ) are formed. Hydrocarbons, mainly from Söderberg-anodes, form tar-aerosols. Dust and soot are also generated. These substances are less important as air pollutants than fluorine compounds, but nevertheless significant. They have great influence upon design of gas collection and cleaning equipment. Data on quantity and composition of these components are scarce, except for sulphur dioxide.

Approximate figures are given in Table 1 below.

Table 1.

Approximate Quantities of Air Pollutants  
Generated During Electrolysis.

Pot type	kg/t Al					
	Solid F	HF	$\text{SO}_x$	CO	Particles	Hydrocarbons
Pre-bake <sup>1)</sup>	8	8	15	200	30-100	negl.
Vertical Stud Söderberg	2	18	15	50 <sup>02)</sup>	20-40	1-3 <sup>2)</sup> 2-6
Horizontal Stud Söderberg	4	16	15	200	20-40	6-10

- 1) Crust breaking between anodes has been claimed to cause a fluoride generation of about 22 kg F/t Al.
- 2) 75% collection efficiency, figures relate to pot exhaust after burner and ventilation air, respectively.

#### Pot Design, Gas Collection and Pot-Room Ventilation.

HSS pots are always covered with individual suction hoods, exhausting large columns of air to prevent hydrocarbon aerosols (tars) from making working conditions in the pot rooms unacceptable.

VSS pots have a gas collection skirt surrounding the anode, collecting a major portion of the fumes evolved in a relatively concentrated form. Most of the hydrocarbons and carbon monoxide in these hot gases is incinerated in a simple burner connected to the skirt.

PB pots were previously designed without separate gas collection systems, usually termed open prebake (OP) pots. Most PB pots installed in recent years are closed (CP) pots with hoods covering the entire pot and providing efficient collection of air pollutants. 95% and more may be collected in modern plants when well operated.

Average collection efficiencies of all systems are less than 100 per cent, a fraction of the pollutants generated will thus always escape into the pot-room atmosphere.

Heat, gases and fumes released from the pots make efficient ventilation of the pot-room very important to the health and comfort of pot-room personnel. The pot-room air is normally exchanged 20 - 40 times per hour.

Data referring to typical conditions are shown in Table 2 below.

Table 2.

Typical Pot Exhaust Rates, Collection Efficiencies and Ventilation Rates for Modern Pot-rooms.

Pot type	VSS	HSS	CP	OP
Exhaust rate, $10^3 \text{Nm}^3/\text{t Al}$	18	275	150	-
Temperature, $^{\circ}\text{C}$	120	50	100	-
Collection Efficiency of Pot Exhaust, %	75	85	95	-
Ventilation rate <sup>1)</sup> , $10^6 \text{Nm}^3/\text{t Al}$	(1.8) 2.2	2.2	1.2	(1.8) 2.2

1) 10-20 $^{\circ}\text{C}$  above ambient at the outlet, depending on energy consumption and rate of ventilation. Brackets refer to scrubbing of ventilation air.

Gas Cleaning and Emissions.

Gases collected at the hoods or skirts of individual CP, HSS and VSS pots are combined in main ducts leading to a gas cleaning installation. A wide selection of wet and dry types of air pollution

control equipment (cyclones, electrostatic precipitators, fabric filters and scrubbers) is used. Recovery of fluorine compounds by sorption on aluminium oxide, which is collected in bag filters, has seen increasing use in recent years, especially with CP and VSS pots. Aluminium oxide and fluorides from the sorption system is fed directly to the pots, the pollutants thus being recycled.

The large volumes of ventilation air limit the choice of gas cleaning equipment to wet scrubbers operating at low pressure drop. Ventilation air cleaning is primarily used at OP and VSS plants, at the latter in combination with pot exhaust cleaning.

A few CP plants have installed ventilation air cleaning in addition to pot exhaust cleaning to meet stringent emission requirements. These plants seem either to have pots with less than about 80% exhaust collection efficiency, or an unfavourable location.

Some examples of typical emissions of fluorine compounds are shown in Table 3. The differences in emissions between plants with no cleaning and plants using the best cleaning techniques are considerable.

During upset conditions at the pots, the differences in emission between uncleaned and cleaned gases will obviously be even greater.

Table 3.

Typical Emissions of Fluorine Compounds from Selected Types of Pots and Gas Collection and Cleaning Systems Operating at Various Pot Exhaust Collection Efficiencies.

Type of Pots	Pot Gas Cleaning	Ventilation Air Scrubbing	Emission of Fluorine Compounds, kg F/t Al (Figures in brackets refer to HF)				
			Collection Efficiency for Pot Gas %				
			0	75	90	95	
VSS	None	None	20 (18)	20 (18)			
	Dry electrostatic precipitator + spray tower	"	20 (18)	5.2 (4.6)			
	"	Spray Screen	2.4 (1.3)	0.8 (0.5)			
	Alumina + bag filter	"	2.4 (1.3)	0.9 (0.6)			
HSS	None	None	20 (16)		20 (16)		
	Floating ball scrubber	"	20 (16)		4.0 (2.3)		
CP x)	None	None	16 (8)			16 (8)	
	Floating ball scrubber	"	16 (8)			3.8 (0.7)	
	Alumina + bag filter	"	16 (8)			1.3 (0.6)	
	"	Spray screen	4.8 (0.4)			0.7 (0.2)	
OP x)	None	None	16 (8)				

At plants having efficient pot gas cleaning and no ventilation air cleaning, modifications of the pot-gas cleaning installations are evidently not going to affect total emissions of fluorine compounds significantly. Maintaining a high collection efficiency or installing ventilation air cleaning is far more efficient. Ventilation air cleaning is especially efficient in reducing emissions of HF. Methods of controlling emissions of particulate fluorine compounds effectively, are also capable of controlling emissions of other solid material and condensed hydrocarbons.

Most smelters operating in the industrialized countries have air pollution control equipment. Only a limited number of smelters have however got the most efficient type of equipment available.

#### Cost of air pollution control.

Costs of air pollution control depend upon the type of pots, cleaning efficiency and other factors. Table 4 shows approximate cost data for plants built in early 1975, based on theoretical calculations. Actual costs may deviate considerably from these data. Costs of installing new control equipment in existing plants are generally much higher than at new plants.

Installed costs of air pollution control at the pot-rooms of CP plants, referring to Table 4, are about 5 to 10% of the total cost of a new plant <sup>1)</sup>.

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1) Assumed to be about US dollars 1.500 per ton annual capacity for a total CP plant including pot-rooms, foundry, carbon plants and facilities. The pot-rooms may account for about one third of the total cost.

Table 4.

Approximate Costs of Gas Cleaning for New Closed Prebake Pots in Early 1975<sup>1)</sup>, Operating at 95% Pot Exhaust Collection Efficiency.

Gas Cleaning Equipment	Emission kg F/t Al (kg HF/t Al)	Installed Cost of Gas Cleaning Equipment, US dollars/t Al Annual Capacity <sup>2)</sup>	Cost of Gas Cleaning, US dollars/t Al Fixed Variable Recovered F Total
Pot exhaust: Floating ball scrubber	3.8 (0.7)	66	17 6 0 23
Pot exhaust: Alumina + bag filter	1.3 (0.6)	89	22 9 -11 <sup>3)</sup> 20
Pot exhaust: Alumina } + bag filter } Ventilation Air: } Spray screen }	0.7 (0.2)	141	35 16 -11 <sup>3)</sup> 40

1) Based on 1970 cost-data from U.S.A., (1), (2), adjusted for price changes. Costs of waste water treatment by addition of lime are included.

2) Hoods and ducts included.

3) Assuming that all F recovered can be returned to the pots.



Operating cost of the air pollution control equipment is about 1 to 5% of the sales prices of aluminium<sup>1)</sup>. Recovery of fluorine compounds reduces costs of gas cleaning significantly. Considered separately, by excluding costs of hoods and ducts which may be regarded as part of the ventilation equipment, recovery is profitable. Cleaning of ventilation air is expensive, and in some cases adds only marginally to the overall cleaning efficiency. It does however provide an extra safety during difficult operational conditions when pot exhaust collection efficiency may be below design level.

#### Effects of Air Pollution in the Environment

##### General.

The main effects are generally assumed to be caused by fluorine compounds, especially hydrogen fluoride (HF). Solid fluorine compounds are not considered that harmful. Effects of other pollutants are less pronounced. (It should however be noted that concentrations of sulphur dioxide in the vicinity of smelters may be significant. This is currently a problem as sulphur content of carbon materials for the aluminium industry increases as demand for low-sulphur fuels goes up.)

Synergism (i.e. fluorine compounds and other pollutants acting together to cause an amplified effect) has been suggested, but does not seem to be well documented.

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1) About US dollars 880/ton in early 1975.

Effects of air pollution by fluorine compounds, where any, are typically confined to areas within very few kilometers from the smelters. Some damage has however, in cases with an unfavourable combination of large emissions and poor conditions for atmospheric dispersion of pollutants, been observed at least 30 kilometers from a smelter. Severe damage is known to occur in the vicinity of some smelters, while others seem to operate practically without any effects on the environment.

Monitoring of susceptible species and, in some cases, also of the concentration of fluorine compounds in air and precipitation, is usually recommended. It has been suggested, as a simple rule of thumb, that significant damage does usually not occur when emission of total fluorine is below 6 - 900 kg F per 24 hours. Such "rules" may obviously be very misleading, but can give an indication of order of magnitude of damaging emissions.

A comprehensive survey of the biologic effects of fluorine compounds in the atmosphere is given in reference (3).

#### Health Effects arising from Non-occupational Exposure

Experience is generally that emission of fluorine compounds does not cause adverse health effects in people living in the vicinity of aluminium smelters. There are however a few reports of health effects on children living close to smelters. It seems that the only demonstrated changes in children exposed to fluorides were in the teeth, mainly mottling and decreased occurrence of caries. The fluoride concentrations in air were in these cases considerably higher than normally found in the vicinity of smelters with reasonably efficient gas cleaning equipment. Available infor-

mation seems to indicate that airborne concentrations of fluorine compounds, which are low enough to produce no plant response, offer a satisfactory margin of protection for man.

Indications of health effects in heavily polluted areas close to some smelters, probably due to a combined effect of fluorine compounds, sulphur dioxide, smoke and tarry matter, have been reported in the literature.

Complaints of people living near smelters may include reduced visibility, soiling, odours (especially from anode baking and Söderberg plants) and noise.

#### Effects on Vegetation.

Damage to vegetation has been reported near a considerable number of smelters. Four types of effects may occur

- a) visible effect (necrosis; injured parts of leaves become discoloured and die)
- b) reduced growth or yield
- c) biological changes of several kinds
- d) accumulation of fluorides.

Absorption of hydrogen fluoride by the leaves is generally considered the primary cause. Several species of conifers, fruit trees and horticultural plants are extremely prone to damage, for instance pine, sweet corn, apricot and gladiolus. Results from research carried out in temperate regions of the world do, as an example, indicate that no damage to the very susceptible species gladiolus, sorghum and conifers occurs when ambient concentration of hydrogen fluoride is below  $0.5 \mu\text{g}/\text{m}^3$ .

Damage can to some extent be related to fluorine content of plant tissue. Susceptible species may show signs of damage with less than 50 ppm F (dry weight basis) in the tissue. Fluorine content should however not be used as a single criterion in evaluating fluoride damage. Knowledge of the fluorine content of plants is valuable as an indicator of fluoride exposure and in ascertaining whether a certain type of plant damage is caused by fluorides or not. It is generally assumed that immature leaf tissues are most susceptible to fluorides.

To our knowledge, there is no specific information available on effects of airborne fluorides on tropical vegetation. One may however anticipate that the ecosystem of a tropical rain forest is comparatively more resistant than those of the temperate and colder regions, due to the much greater number of species.

#### Effects on Animals

Herbivores may be affected by excessive quantities of fluorine compounds in their diet. It is believed that most of the effects is caused by fluorine compounds assimilated by the plants. Solid fluorine compounds adhering to the surface of the grass or hay, are probably far less important. Young animals are particularly vulnerable during teeth formation. Skeletal damage due to prolonged exposure is the most common effect on adult animals.

The response of cattle to excess fluorides in the diet may be:

1. Reduced appetite.

Occurs when fluoride content of the diet is high during a short period. Cattle may tolerate 100 ppm F (dry weight basis) in the total diet for 30 days.

2. Effects on teeth.

Effects are determined by fluoride content of the diet during teeth formation. No significant damage occurs when the total diet contains less than 30 ppm F in this period.

3. Accumulation of fluorides in the skeleton.

Fluoride content of bone material will always increase with time. Detrimental changes may occur when accumulated amounts exceed about 5000 ppm F. Detrimental accumulation will probably not be reached if the diet contains less than 30 ppm F.

The data referred to above represent a simplification of real situations, for instance in the sense that well-fed cattle may be more resistant.

Fluoride ingestion by cattle can be determined by chemical

analysis of fluoride excretion in the urine. Accumulated quantities can be determined from biopsy of tail or rib bones.

### 3.1.3. Water Pollution

Several smelters use scrubbers for cleaning gases. Liquid effluents from scrubbers are the most significant potential water pollutants from aluminium smelters. The effluents contain fluorine compounds, solids and, at Söderberg plants, hydrocarbons. In addition, there are modest quantities of cooling water.

Many plants located in-land recycle scrubbing liquor in a closed system. Pollutants are recovered or removed from the liquor as a sludge by precipitation with lime and dumped. The main problem of cleaning effluents is to reduce the content of hydrocarbons, among them tarry matter and phenols, in scrubbing liquor from Söderberg plants.

Several coastal plants discharge untreated or neutralized scrubbing water. Hydrocarbons in effluents from Söderberg plants are the major environmental concern in this case, as open sea-water recipients have a large capacity for acids and a fairly high background concentration of fluorides. Coastal plants in many countries will probably have to clean

their liquid effluents in the future.

#### 3.1.4. Solid Wastes.

Solid wastes from smelters may be classified as:

1) Spent pot linings.

Pots normally have a service life of 2-4 years. Linings must then be renewed and the discarded ones dumped or treated to recover materials, particularly fluorine compounds. Linings are the major quantity of solid waste, about 40-90 kg per ton Al produced.

2) Anode butts from pre-bake pots.

Normally recycled to anode plants.

3) Miscellaneous solid wastes.

Includes dust from gas cleaning equipment, sludges from cleaning of scrubbing water, dross from skimming of pots, spills from materials handling and other kinds. These wastes may be dumped or subject to recovery.

Dumping of solid wastes is still common practice. Environmental considerations and rising prices of fluorine compounds are causing an increase in recovery. Dumping at sea is, at least

in some cases, causing no visible damage to marine life. There are however indications of accumulation of hydrocarbons in organisms in the dumping areas. Current trends to restrict ocean dumping of wastes in general will probably force most aluminium plants to find other ways to dispose of solid wastes.

Land-fills of spent pot linings are subject to spontaneous ignition and make poor building ground due to disintegration. All wastes placed upon land-fills may cause air pollution, due to wind-borne dust, and water pollution, because of leaching by precipitation.

Foundry wastes are normally re-melted to recover metal and electrolyte for the pots. Dust from gas cleaning equipment may be returned to the pots, provided it does not contain excessive amounts of impurities. Spent pot-linings may be treated to recover fluorine compounds, carbon, scrap iron or heat. Several recovery processes are used, but the majority of plants are still not recycling pot linings.

#### 3.1.5. Working Conditions in the Pot Rooms.

Working conditions in pot-rooms tend to be unpleasant, and in some cases unhealthy, due to a number of factors, such as:



Shift work

Exposure to polluted air

Heat exposure

Draught

Noise

Dirt

Poor light

Heavy work

Accidents

The quality of the working environment varies considerably between plants, owing mainly to design of pots and pot-rooms, ventilation and operational procedures. New plants tend to offer better working conditions than old ones, and many companies take great care to design their plants for good working conditions. Fluorosis is normally not a health problem at modern plants. Pot-rooms with closed prebake pots have better general atmospheric conditions than others. Heat exposure may be a problem in several cases, for instance for people working between closely spaced pots.

Many companies are regularly monitoring physical working conditions. Analysis of the pot-room atmosphere to determine concentrations of dust, fluorine compounds, sulphur dioxide and tar is frequently done. The results are compared with TLV (see Table 10) and evaluated in connection with other relevant factors to obtain a measure of the exposure of the individual workers. Medical examinations are frequent, usually including chemical analysis of fluoride content of urine which serves as a measure of total fluoride burden.

Improving working conditions is important to protect the health and well-being of the present employees and to attract qualified people for future employment.

Internal working conditions in the pot-rooms is one of the most pressing environmental problems of the industry.

### 3.2 Foundry Operations.

Molten metal from the electrolysis is normally transferred to the foundry department of the smelter for purification, addition of alloy components and casting to semi-finished products (ingots, billets etc.).

Chlorine fluxing is still widely used to purify the metal, and may cause evolution of fumes containing aluminium chloride ( $AlCl_3$ ). Similar fumes are produced in dross furnaces, used for recovery of aluminium from skimmings and miscellaneous wastes. The fumes are normally cleaned in scrubbers or filters. Non-chlorine treatments such as nitrogen treatment under flux, followed by filtration, are becoming more important these days. Some plants remove dissolved gases from the metal by vacuum treatment, thus avoiding chlorine fluxing.

Moderate quantities of water are used for scrubbing of furnace fumes and quenching of moulds. Effluents from the quenching contains lubricants, partially decomposed.

Heat requirements in the foundries are mostly covered by fossile fuels, and contribute to emissions of sulphur dioxide.

### 3.3 Production of Carbon Cathodes and Anodes.

Preparation of carbon cathodes, anode paste and prebake anodes for the pots is carried out at a separate carbon plant, frequently on the smelter site.

Anthrasite, calcined petroleum coke and pitch are the most important raw materials. In addition, butts from pre-bake anodes are normally recycled to the anode plant. Carbon plant operations generally include crushing, drying, grinding, classifying and mixing.

Anodes for pre-bake pots and carbon blocks for cathodes are calcined at about 1100-1200°C. Odorous hydrocarbons and fluorine compounds from anode butts are liberated during the process.

Flue gases from anode baking may be cleaned by electrostatic precipitators, removing condensed hydrocarbons and thus reducing visible emissions. The precipitators have to operate at comparatively high temperature, a fraction of the hydrocarbon will thus be in vapour state and emitted. Emission of fluorine compounds is caused by recycled anode butts. Electrolytic bath adhering to their surface is partially removed by manual cleaning, emission thus depending on the efficiency of this operation. Available data on emissions from anode baking plants are scarce. Data from two plants, equipped with electrostatic precipitators, indicate an emission of 1 kg of total F per ton of anodes produced. One plant, believed to have one of the most efficient control systems operating in the world today, has an electrostatic precipitator, a venturi scrubber and a spray tower in

series. The emission is less than 0.15 kg total F per ton anodes produced. A new process, featuring adsorption of fluorides and hydrocarbons on aluminium oxide, is claimed to be very efficient. Hydrocarbons are removed by incineration before the aluminium oxide, fluorine compounds still adsorbed, is fed to the pots.

Anode paste for Søderberg pots and paste for cementing cathode blocks together are prepared at lower temperature. Pitch smelting may cause moderate emissions of hydrocarbons from these plants.

Solid material from mechanical operations may be captured in cyclones and textile filters and returned to the process. Emissions are low and not significant to the environment, except very close to the plant.

#### 3.4 Miscellaneous Operations.

Local dust problems may occur during loading and handling of raw materials and dust precipitated in air pollution equipment.

Local problems, mostly of an occupational hygiene character, may arise during operations such as anode rodding, demolition of old pots and cleaning of pre-bake anode butts prior to recovery of carbon.

Fluorine compounds to be added to the pots are generally produced in plants located independently of the smelters. Several smelters do in addition recover considerable amounts of cryolite or aluminium fluoride from flue gases and wastes. Emissions from these activities are generally low compared with those from the reduction plant.

#### 4. FABRICATING

A large number of processes is used in fabricating. Table 5 shows some main processes and associated problems of pollution. Remelting of process scrap, frequently carried out in the fabricating plants, is covered in section 5.

Table 5.

Some Main Products and Processes in Fabricating Plants, and  
Associated Problems of Air and Water Pollution.

<u>Product</u>	<u>Process</u>	<u>Air pollutants</u>	<u>Water pollutants</u>
<u>Forming</u>			
Plate, coil and wire <sup>1)</sup>	Hot rolling	Water vapour and oil fumes	Oil-water emulsions
Sheet, strip and fcil	Cold rolling	Oil mists	Spent lubricants
Slugs	Punching	Lubricant fumes	
Profiles, Tube, (wire)	Extrusion		Quench water Alkaline solutions
-----			
<u>Surface finishing</u>			
Anodized sheet, profiles, con- sumer goods etc.	Chemical etching, anodizing and colouring		Alkaline and acid solutions containing aluminium. Solutions containing chromium and other inorganic and organic compound used for colouring.
Litographic sheet	Chemical and electrochemical etching, anodizing and sealing		Alkaline and acid solutions contain- ing aluminium
Painted sheet etc.	Chemical etching, paint- ing, printing in some cases	Hydrocarbon aerosols from paint baking	Alkaline and acid solutions contain- ing aluminium

1) Frequently preceded by continuous casting.

Spent emulsions, mainly from hot rolling, may require compli-  
cated treatment for separation in oil and water suitable for  
discharge. Alkaline and acid solutions may be combined and pH

adjusted for precipitation of aluminium hydroxide. Metals used in chemical surface treatment can be precipitated as hydroxides. Hydrocarbon aerosols from paint baking ovens can be eliminated by incineration at about 800°C.

## 5. SCRAP PROCESSING.

Recycling of discarded aluminium articles and a fraction of the scrap arising during fabrication of aluminium products is carried out by the secondary aluminium industry. Given the rapid increase of primary production in past years, and an average life-time of several years for aluminium goods except cans and other packaging, the amount of scrap from discarded articles is small compared to primary production.

Several types of scrap need pre-treatment prior to melting, to remove moisture and contaminants such as oil or paint. Pre-treatment consists of heating, creating fumes, or washing, creating polluted water. The effluents can be cleaned by conventional means.

Melting and refining of scrap can be carried out in several types of furnaces. Melting of finely divided aluminium scrap, and magnesium removal in refining operations, creates emission problems which are specific to the secondary aluminium industry.

Recovery of finely divided scrap requires the molten aluminium to be protected by a flux of molten salts. Fumes can be cleaned by conventional means, bag filters have proved successful.

Magnesium removal from scrap is frequently required to produce alloy suitable for casting. This is done by introducing chlorine to the melt to form a melt of magnesium chloride. Excess chlorine



reacts with aluminium to form an obnoxious fume of aluminium chloride, which has to be removed by filtration or scrubbing with water. The fume problems can be largely eliminated by a process modification, based on careful introduction of the exact quantity of chlorine required. A similar process can be adapted in the foundries of the primary smelters.

## 6. LEGISLATION AND REGULATIONS

### 6.1. Introduction.

Many countries have general legislation to curb pollution from industry, for instance limiting emission of dust. Such legislation is applicable to the aluminium industry, but several countries have in addition introduced specific regulations for the fluoride problems of the primary aluminium smelters. Only this type of legislation is considered here.

As the situation is changing rapidly, some of the data in this section may be obsolete.

A survey of regulations is given in reference (4).

### 6.2 Emission.

The meaningful measure of emission of fluorine compounds from a plant, from an environmental point of view, is mass per time unit, for instance kg F per hour, rather than concentration of fluorine compounds or percentage cleaning efficiency. The quality of emission control is logically measured as specific

emission, as kg F/t Al produced. Regulations specifying a certain specific emission should, from consideration of the receiving capacity of the environment, be related to plant size to limit overall emission. Plant size is however frequently not considered directly in the emission regulations, but taken into account indirectly by regulations concerning fluoride concentrations in ambient air or biological material. Several countries require the best practicable cleaning technology to be used, regardless of plant size.

Some countries specify the emission as hydrogen fluoride, while others use total fluoride. (As already pointed out, hydrogen fluoride is regarded as the most harmful constituent of emissions.)

Examples of strict regulations are shown in Table 6.

Table 6.Examples of Regulations Applied and Applicable to Fluoride Emissions from New Primary Aluminium Smelters.

Country (Province)	Type of Regulation
USA, Proposed Federal Standard	<p>Emission of total fluoride from smelter and anode plant in combination shall not exceed 1 kg total F per ton aluminium.</p> <p>Emissions shall not exceed 10% opacity.</p>
W. Germany	<p>Emissions of gaseous fluorine compounds shall be reduced as much as feasible. Examples of emissions from new smelters with closed pre-bake pots: 0.7/0.9/1.2 kg gaseous F/tAl, respectively.</p>
Japan (Kagawa)	<p>1.0 kg gaseous F/tAl regardless of capacity.</p>
Norway	<p>Smelters are considered individually. Maximum emission at the most recent VSS plant is 1.0 kg total F/t Al. Maximum emission at the most recent CP plant is 1.3 kg total F/t Al.</p>

6.3 Ambient Air.

Air quality standards or guidelines for fluorine compounds have been introduced in some regions of the world. Recent regulations seem to consider only hydrogen fluoride, maximum concentrations in air are in the order of magnitude of one microgram per m<sup>3</sup> or less. Some examples are shown in Table 7.

Table 7.Ambient Air Regulations for Fluorides.

Country	Concentration, µg/m <sup>3</sup>	Averaging Time
USA (Oregon/Washington)	3.7 (HF)	12 hours
	2.9 (HF)	24 hours
	1.7 (HF)	7 days
	0.84 (HF)	30 days
USA (Pennsylvania)	5 (HF)	24 hours
W. Germany	2 (gaseous fluorides)	Long time exposure
	4 (gaseous fluorides)	Short time exposure

It should be kept in mind that damage from existing smelters can primarily be reduced by improving installations for gas collection and cleaning. Increasing stack heights and modifying local practice of agriculture and forestry may in some cases be useful. The main purpose of the stacks, where appropriate, is to disperse residual emissions and to avoid high ground level concentrations in periods when operational problems at the smelters cause emissions which are larger than normal.

Damage from future plants may, in addition, be prevented by selecting sites having good atmospheric dispersion conditions, low background pollution, resistant natural vegetation and no susceptible agriculture. The connections between emissions, dispersion, absorption and biological response have so far proved too complex for accurate prediction of environmental effect from future smelters.

#### 6.4. Vegetation.

Maximum acceptable concentrations of fluorine compounds in forage and animal matter are being used in some countries, as a supplement or substitute for air quality regulations.

Some data are shown in Table 8.

Table 8.Maximum Fluoride Content of Forage in Washington, USA.

Period	Fluoride content shall not exceed ppmF, dry weight
Average for any 12 consecutive months	40
Each month for more than 2 consecutive months	60
More than once in any 2 consecutive months	80

The World Health Organisation (WHO) has recommended a maximum tolerable level of 50 ppm for exposures lasting 6 months or more.

6.5. Liquid Effluents.

Some countries have specified maximum concentrations of fluorine compounds in waste water.

More comprehensive regulations are given in USA, data are shown in Table 9.

Table 9.

36.

Interim Effluent Limitation Guidance, US. Federal Government.

Component	KgF <sup>-</sup> /tAl	
	Now	After 1977
Fluoride (F <sup>-</sup> )	5.0	0.35
Total suspended solids	5.0	0.5
Oil and grease	2.5	0.25

6.6. Working Atmosphere.

Many countries have adopted the values given in Table 10.

Table 10.

Threshold Limit Values (TLV) for Some Compounds Occuring in the Working Atmosphere at Aluminium Smelters (5).

Compound	TLV, mg/m <sup>3</sup> <sup>1)</sup>
F <sup>-</sup>	2.5
HF	2
SO <sub>2</sub>	13
CO	55
Coal tar pitch volatiles	0.2
Inert dust	10

1) 760 mm Hg and 25°C.

The USSR recommends more strict levels, 0.7 mg HF/m<sup>3</sup>  
and 1.0 mg total F/m<sup>3</sup>.



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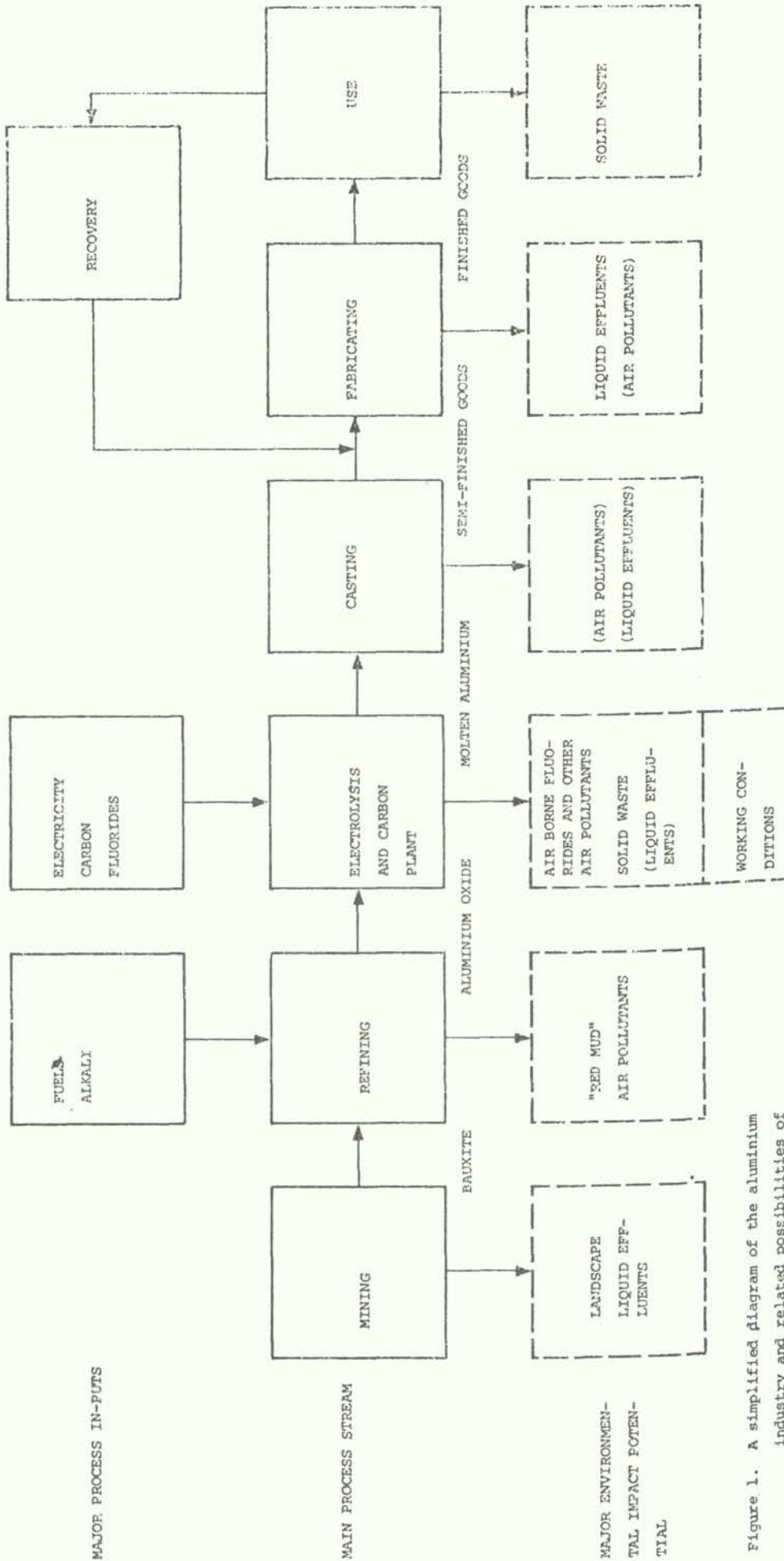


Figure 1. A simplified diagram of the aluminium industry and related possibilities of environmental impact.

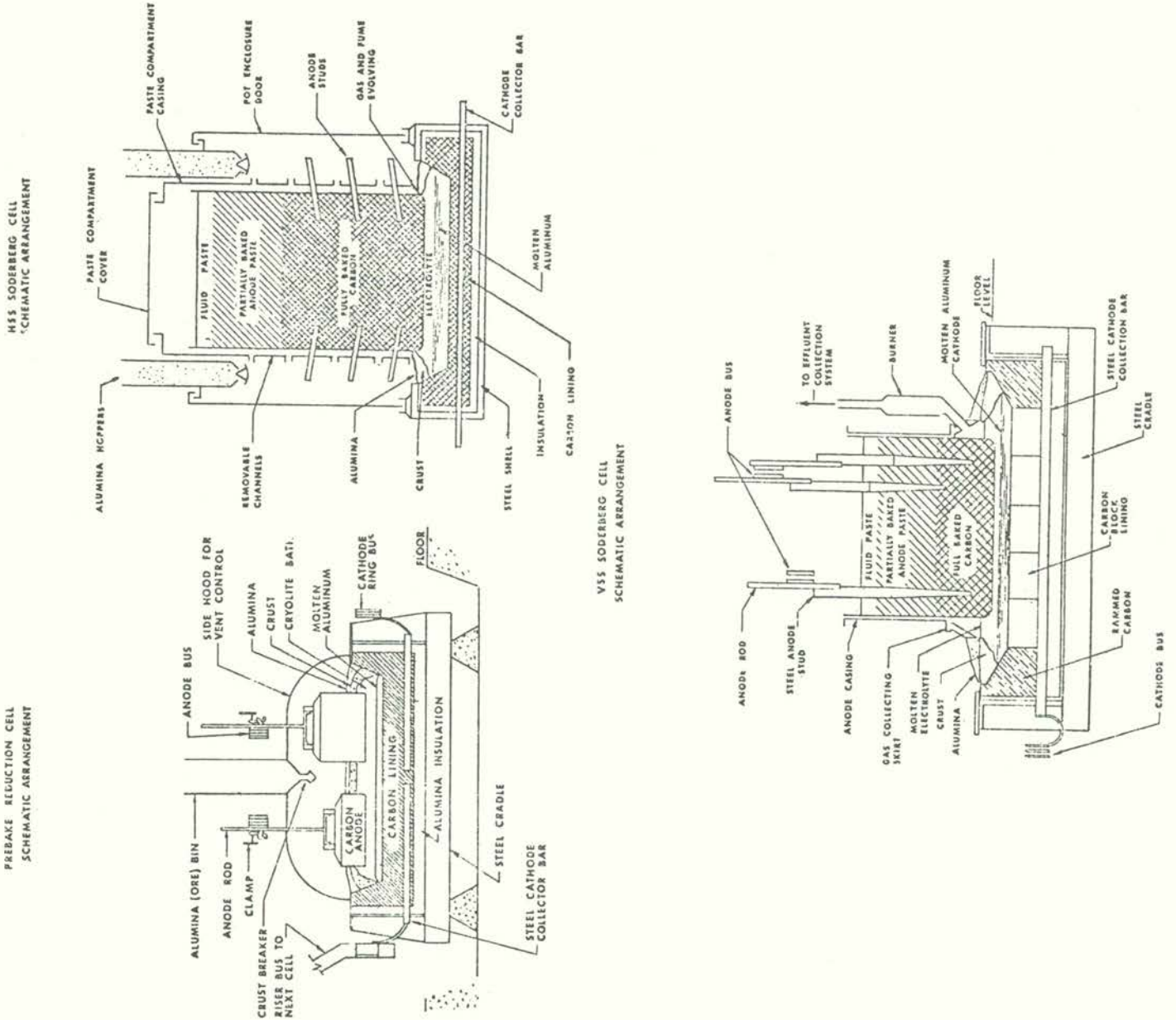
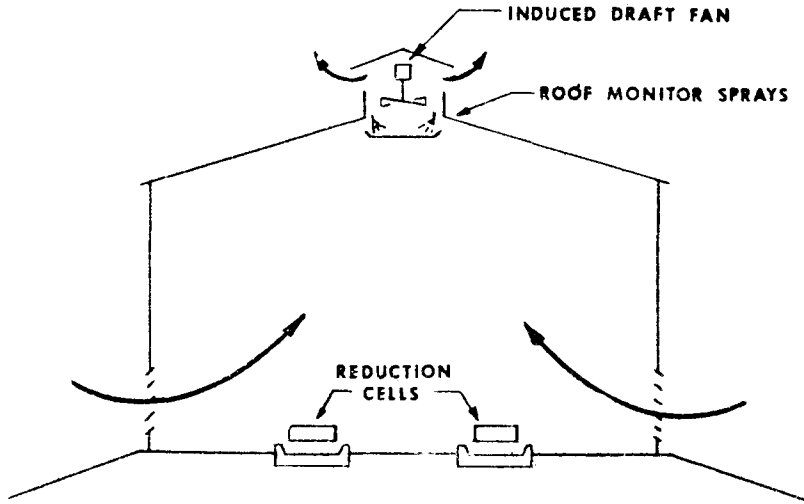


Figure 2. Examples of main types of aluminium reduction pots (1).

The prebake pot shown features crust-breaking and feeding of aluminium oxide between anodes. Other types have closely spaced rows of anodes, crust-breaking and feeding taking place between anodes and the cathode.

ROOM COLLECTION SYSTEM SIDEWALL ENTRY



ROOM COLLECTION SYSTEM BASEMENT ENTRY

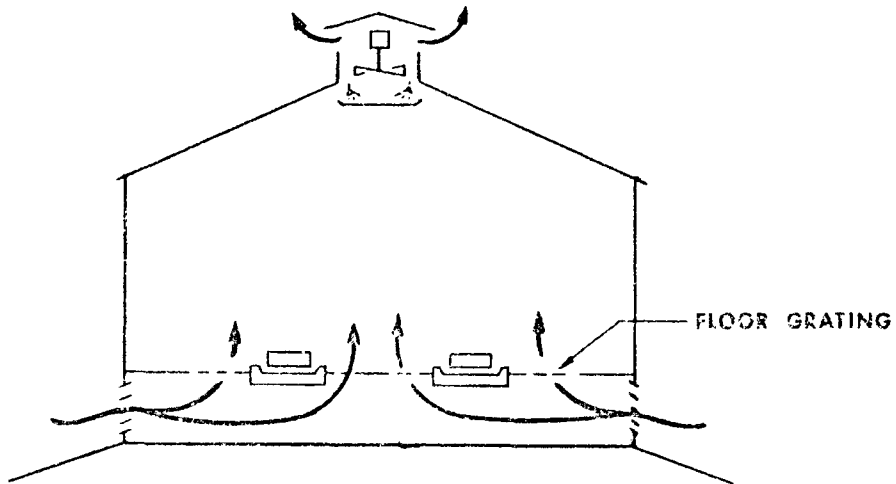


Figure 3. Examples of pot-rooms with ventilation air cleaning (1).

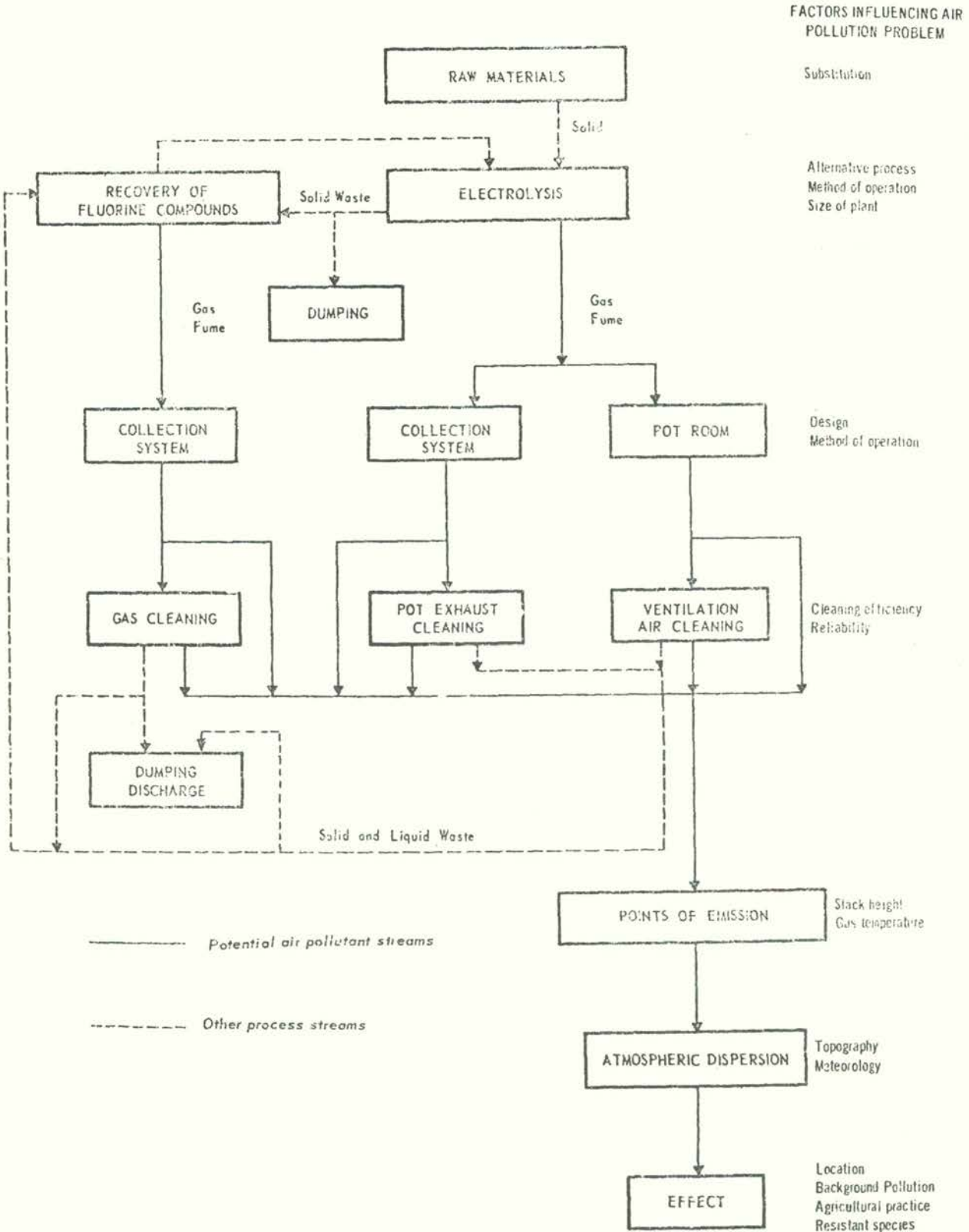


Figure 4. Structure of the air pollution problems caused by fluorine compounds in the primary aluminium smelting industry (2).



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RESOURCES AND ENERGY  
IN ALUMINIUM PRODUCTION

Report prepared for UNEP

by

Merton C. FLEMINGS ( U.S.A. )

October 6, 1975

Resources and Energy in Aluminum Production

by

Merton C. Flemings\*

Introduction and Summary

Aluminum is used in a wide range of applications because of its low density, high strength-to-weight ratio, resistance to corrosion, high electrical conductivity, ease of fabrication, and ease of recyclability. The total annual world production of the primary metal in 1973 was in excess of 13 million tons. Output over the last ten years increased at an annual growth rate of about 8 percent, resulting in a doubling time of about 9 years. Consumption of aluminum metal is higher than the production of primary metal because of recycling through the secondary industry. Typically, this recycling yields about another 25 percent available aluminum metal.

Aluminum is the most abundant metal in the earth's crust (7%) and alumina ( $\text{Al}_2\text{O}_3$ ) is the principal raw material for aluminum metal production. All igneous rock contains silicates of aluminum and upon weathering the aluminum usually remains insoluble in the form of an impure aluminum silicate, a clay. Certain of the clays may some day be used for production of alumina metal but at the present time, the only commercial source of the alumina used for aluminum metal production is the mineral bauxite. World reserves of bauxite

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\* Ford Professor of Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A. Paper to be presented at the Aluminum Seminar of the United Nations Programme, Paris, October 6-8, 1975.

are estimated at about 6000 million metric tons. These are primarily in Australia (with 35 percent of the world reserve known), Guinea (20 percent), Jamaica (10 percent), Hungary and Yugoslavia (10 percent) and Surinam and Ghana (10 percent).

Bauxite can contain 30 to 60 percent alumina, 1-15 percent silica, and 1-30 percent iron oxide. After mining, the first step in production of aluminum is purification of this ore by the traditional Bayer Process to alumina ( $Al_2O_3$ ). The alumina is then reduced electrolytically by the Hall-Herroult Process to aluminum metal. Thereafter, it is alloyed, cast into ingots and subsequently formed by processes such as casting, rolling, forging or extrusion.

Primary aluminum production is a high consumer of electrical and thermal energy, although on a per unit volume basis, the energy required is comparable to other nonferrous metals, such as copper. By far the largest percentage of energy is consumed in the electrolytic reduction step. The energy breakdown is as follows:

	<u>Percent</u>
Bauxite mining, treatment and transport	1-2
Alumina manufacture	12-16
Aluminum reduction	64-68
Remelt and fabrication	16-20



Electrical energy consumed in production is significant, it comprises about 70 percent of the industry's usage, measured in thermal units. In the United States in 1973, 83.6 billion KWH were used by the industry, or about 4 percent of the total electrical energy consumed by the country. Process improvements have resulted in a steady decline in required KWH per ton of aluminum, but the continuing increase in utilization of aluminum means that total energy requirements for aluminum production will continue to grow.

By application of available technology, and improvement and modernization of plants and equipment, the present average energy consumption of the aluminum industry (per pound of metal produced) could be reduced by something like 30 percent. However, the capital investment necessary to achieve this reduction is very large indeed. Within the next 4 to 5 years a reduction of 10 percent appears to be about the maximum feasible. This 10 percent reduction (from 1972 levels) has been established as a goal of the U.S. industry following a series of government-industry meetings in the second half of 1974.

Because aluminum constitutes so much of the earth's crust there is no danger whatsoever of running out of a supply of available raw material. However, the supply of high grade bauxite is limited and so other sources of aluminum will no doubt be used eventually, at least by countries such as the United States which have virtually no domestic bauxite. The energy cost of producing

metal from such ores will be somewhat higher than that of producing metal from bauxite.

A most important aspect of resource conservation in aluminum production is re-cycling. Recycling of aluminum requires only a small percentage of the energy to produce the same metal from virgin sources and very large amounts of aluminum scrap are potentially available for recycling. In the U.S., a total of 1.1 million tons of aluminum scrap were recycled in 1972, 80 percent being "new" scrap and the remainder "old" scrap. An outstanding problem, belatedly receiving national attention is this "old" scrap.

#### Production of Alumina from Bauxite

Alumina is extracted from bauxite by digestion at elevated temperatures (300-400°F) and pressure with a strong caustic soda solution resulting in a sodium aluminate liquor and a residue termed "red mud". The red mud consists of silica, boron oxide, titanium oxide and insoluble aluminum silicate. The pregnant alumina liquor is cooled and seeded with crystals of alumina trihydrate. About half the alumina precipitates over a 36 to 100 hour period as alumina trihydrate. The precipitate is then filtered and washed, while the filtrate, consisting of a weak solution of sodium aluminate and caustic soda, is recycled after the excess water is evaporated. Table 1 is a process diagram for the Bayer Process showing the points of heat input and output.

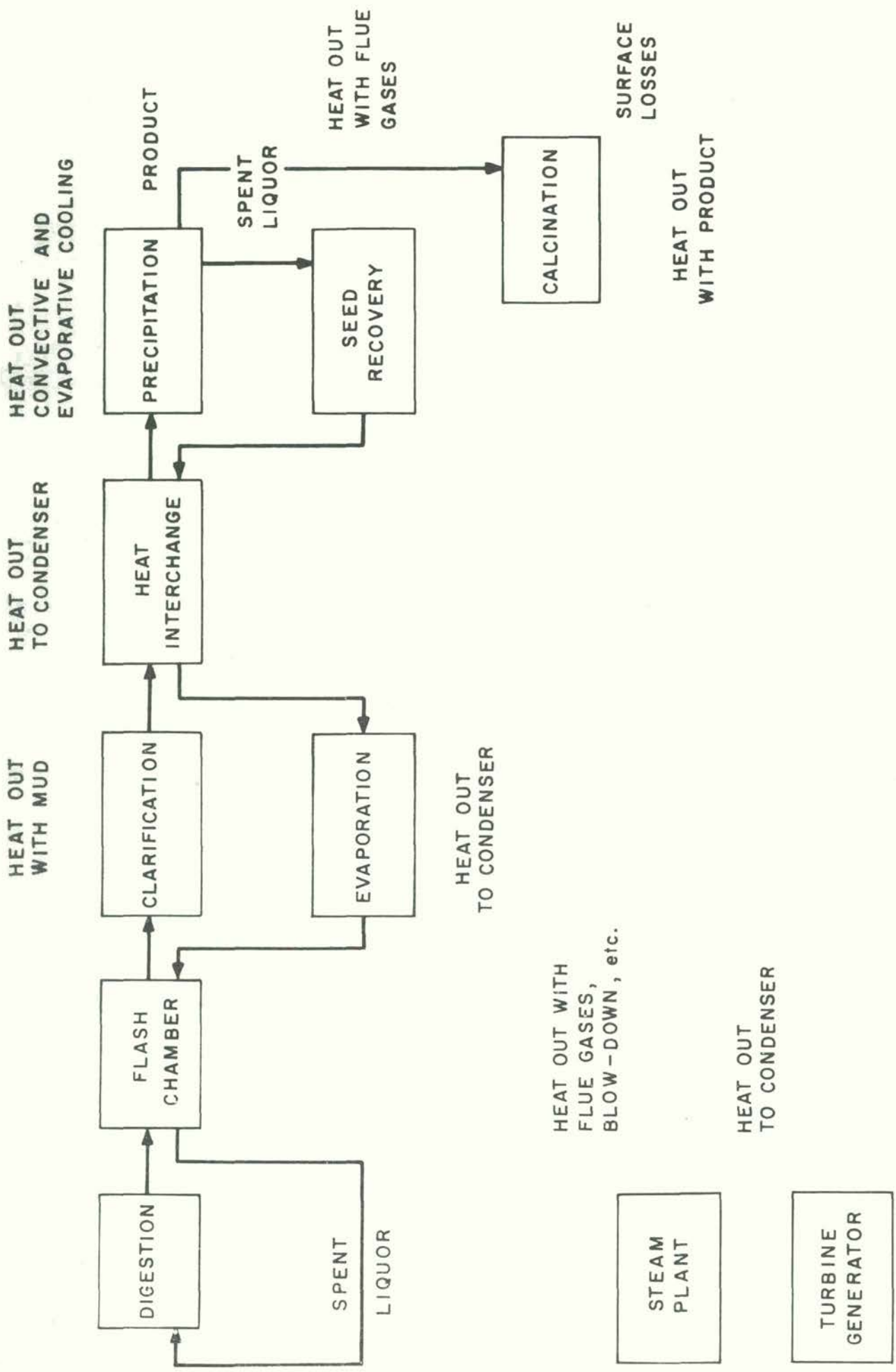


TABLE I  
 BAYER PROCESS HEAT DIAGRAM (FROM CUNDIFF)

In the traditional process the crystalline alumina trihydrate is calcined in a rotary kiln at 2000°F to remove the water, resulting in pure crystalline alumina. A recent energy saving advance in technology is the "Flash Calciner" introduced by Alcoa to replace these rotary kilns. This flash calciner is a fluidized bed that utilizes modern dispersed phase technology to improve heat exchange and reduce radiant levels. It reduces energy consumption per metric ton of alumina from  $4.4 \times 10^6$  to  $3.08 \times 10^6$  BTU's, or 30 percent. The theoretical energy required to drive the water from alumina trihydrate is  $2.63 \times 10^6$  BTU's so waste heat is reduced from  $1.87 \times 10^6$  to  $.55 \times 10^6$  BTU's per ton. The reduction in energy is 1 percent of the total required to produce a ton of fabricated aluminum.

#### Aluminum from Non-Bauxitic Sources

Because of the absence of sufficient bauxitic ores in countries that are large consumers of aluminum (notably the United States and U.S.S.R.) there has been substantial interest in developing economical methods of producing aluminum from non-bauxitic sources. The United States, for example, produces about 34 percent of the world's aluminum and to do this, it imports about 90 percent of the ore needed. Yet it possesses over 160 billion tons of alumina in sizeable deposits of anorthosite, clay, laterites, shale, and low grade bauxites. Also, large deposits of alunite, overlooked in previous explorations are now being

reported. These ores contain typically 14-20 percent aluminum compared with the 25 percent aluminum in a high grade bauxite. Some of the ores being considered for possible ultimate use are listed in Table 2.

At the present time it is not economical to extract aluminum metal from these non-bauxitic or low grade bauxitic ores. However, substantial work is ongoing in the United States under sponsorship of the Bureau of Mines and in a joint Bureau of Mines-industry effort to develop and test the economical viability of processes to permit exploitation of these ores.

Some of the more favorable processes (from an energy standpoint) for producing  $Al_2O_3$  from these ores are listed in Table 3. The best of these involves 2.4 times the energy required to produce the equivalent amount of  $Al_2O_3$  from bauxite. It should be recalled, however, that the energy for obtaining  $Al_2O_3$  is less than a fifth of the total energy for producing aluminum from bauxite. Several of the processes appear within reach of economic reality, being currently estimated at only 20 percent higher than the Bayer/bauxite process.

#### Electrolysis of Alumina

Because the electrolysis consumes such a high fraction of the total energy to produce aluminum (>60%) this step is usually done in locations that are (or were originally) locations of relatively cheap electric power. In this step (the "Hall-Herroult Process") the aluminum is electrolyzed in a molten cryolite bath at a temperature of 1760-1800°F. The reduction cell is made of a carbon-lined box containing a pad of molten cryolite in which the

TABLE 2  
ALUMINUM ORES  
(From Higbie)

<u>MATERIAL</u>	<u>FORMULA</u>	<u>% Al</u>	<u>% Al<sub>2</sub>O<sub>3</sub></u>	<u>TONS TON Al</u>
ALUMINA	Al <sub>2</sub> O <sub>3</sub>	53	100	2
BAUXITE		25	47	4
Boehmite	Al <sub>2</sub> O <sub>3</sub> · H <sub>2</sub> O			
Diaspore	Al <sub>2</sub> O <sub>3</sub> · H <sub>2</sub> O			
Gibbsite	Al <sub>2</sub> O <sub>3</sub> · 3H <sub>2</sub> O			
CLAY		20	38	5
Kaolinite	Al <sub>2</sub> O <sub>3</sub> · 2SiO <sub>2</sub> · 2H <sub>2</sub> O			
SHALE	Impure Clay	15	38	7
ANORTHOSITE		14	27	7
Albite	Na <sub>2</sub> O · Al <sub>2</sub> O <sub>3</sub> · 6SiO <sub>2</sub>			
Anorthite	CaO · Al <sub>2</sub> O <sub>3</sub> · 2SiO <sub>2</sub>			
ALUNITE	K <sub>2</sub> SO <sub>4</sub> · Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 2Al <sub>2</sub> O <sub>3</sub> · 6H <sub>2</sub> O	20	87	5
DAWSONITE	Na <sub>3</sub> Al(CO <sub>3</sub> ) <sub>3</sub> · 2Al(OH) <sub>3</sub>	19	33	5

TABLE 3

PROCESS ENERGY CONSUMPTION FOR ALUMINA PRODUCTION

(From Higbie)

<u>Process</u>	<u>10<sup>6</sup>BTU/Metric Ton Al<sub>2</sub>O<sub>3</sub></u>	<u>Ratio to Bayer</u>
Bayer/bauxite	16.2	1.0
HNO <sub>3</sub> -Ion exchange/clay	52.0	3.2
HCl-Ion exchange/clay	38.5	2.4
Sulfurous acid/clay	42.0	2.6
Lime-soda sinter/anorthosite	51.0	3.1
HNO <sub>3</sub> -Pressure leach/clay	52.0	3.2
HCl-Isopropyl ether/clay	45.0	2.8

alumina is dissolved. The anode is a single large block or several small blocks of carbon. The alumina is reduced to aluminum at the cathode and the carbon is oxidized to carbon dioxide at the anode. Figure 1 is a cross section through a modern reduction cell. In a typical modern cell the box might be 9m long by 3.5m wide, and 1.2m deep. The cavity within the carbon blocks which contain the molten cryolite and aluminum might be 8 x 3 x .6 m.

Current efficiencies in these cells range from 85 to 90 percent, due to material losses of the metal and re-oxidation of aluminum by the  $O_2$ . Voltage efficiencies are low (around 40%) due to electrode resistance, polarization and radiation heat losses. As a result, overall power efficiency is about 45 percent.

During the past three decades the electrical energy consumed in this process has been cut nearly in half, by improving the efficiency of the Hall-Herroult process. Power consumption has been reduced from an average of 27 to 17 KWH/Kg of metal produced, and to 14.3 KWH in today's most efficient smelters. The theoretical minimum energy required to reduce alumina is about 7.9 KWH/kg and so the average energy efficiency of industrial smelters is about 45 percent, with the best operating at about 55 percent efficiency.



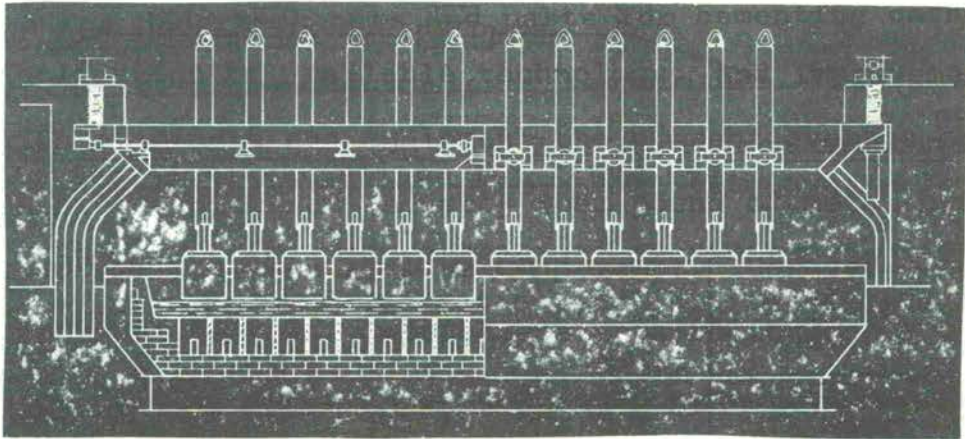


Figure 1: Cross section of a modern reduction cell showing multiple anodes (from Smith).

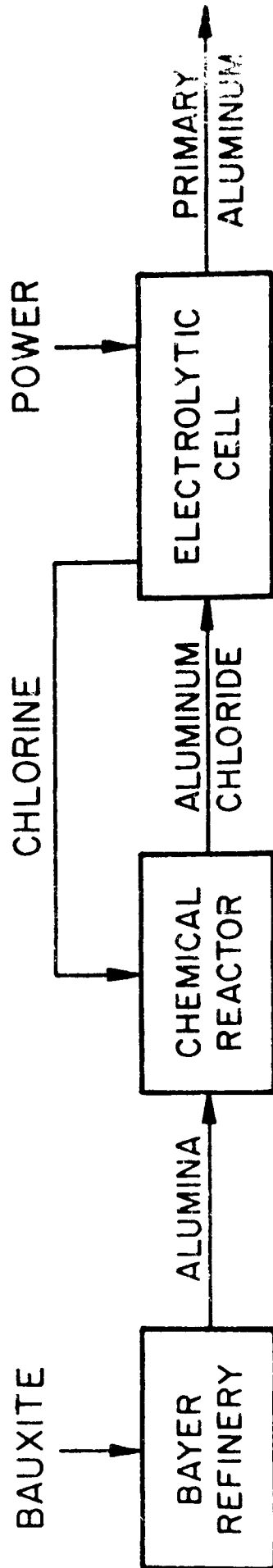
Clearly the greatest potential for energy saving in production of metal from the ore lies in this electrolytic step. This is both because it consumes by far the largest fraction of the energy required to make aluminum, and because the efficiencies are still relatively low. Energy savings can be made in three ways:

1. Replacing less efficient equipment with modern cells capable of achieving about 14.3 KWH per Kg thereby reducing the industry average requirement from its current 17 KWH per Kg.
2. Research and development to introduce new technology to reduce the energy requirement in the Hall-Herroult cell below the best now achieved in practice of about 14.3 KWH per Kg. (One aluminum company has reported achieving values as low as 12.5 KWH/Kg in its newest experimental cell.)
3. Introduction of new more efficient processes to replace the Hall-Herroult cell.

Regarding the last point, many new processes have been studied by the industry in attempts to find a less costly means of producing aluminum from alumina. Of these, the most developed appears to be the Alcoa chloride process. In this process (Table 4), alumina is combined with chlorine in a reactor, forming aluminum chloride. The aluminum chloride is then electrolytically

TABLE 4

ALCOA SMELTING PROCESS



processed in a completely enclosed cell, and the chlorine and aluminum separated. The chlorine is recycled to the reactor in a closed loop. It is anticipated that only 10 KWH/Kg of product will be required for this process. This represents a 30 percent reduction of energy from the most efficient smelter using the Hall-Herroult process. It represents a cell energy efficiency of about 80 percent.

#### Remelting, Fabricating and Finishing

Remelting, fabrication and finishing comprises only a relatively small part of the energy cost (16-20%) of producing aluminum. Nonetheless, significant energy savings can be achieved here.

The largest single saving is achieved by avoiding remelting altogether, taking liquid metal from the cells and feeding it directly to large off-site customers, being trucked as much as 300Km.

When remelting is required, as with scrap, it is usually done (in primary aluminum plants) in oil or gas fired open hearth furnaces which achieve a maximum production rate of about 7-1/2 metric tons/hr. Fuel efficiency is about 30 percent. Substantial room for improvement exists here both in terms of production throughout the furnace and in energy utilization.

Flow of metal through remelt and fabrication is shown in Table 5. The two percent metal loss figure may appear small until it is put into perspective. The total loss in energy, including heat and the value of the metal which must be replaced is 6.7 million BTU/ton.

Melting loss in part originates from the oxide films around and in solid charge components. A material called "skim" floats on the melt surface which starts after initial melting as a material of 99+% metal and less than 1 percent oxide. It is also formed during uncontrolled metal transfer and during fluxing for metal clean up purposes. During melting, oxidation takes place in this layer resulting in a loss of high-energy content metal.

Industry practice has been to remove skim and treat it by secondary processes to recover metal. As removed from the furnace, the skim may contain 50-90 percent metal. During removal, reclamation, and subsequent cooling, the mass can undergo further metal oxidation which can be equal to or even greater than that in the furnace operation. Most treatment processes are far from ideal and metal recoveries can range from 0 - 60 percent with an average by those carrying out such processes being perhaps 30 percent. New and better processes for treatment are needed. The end product of this sequence is generally called dross. Metal can be and is recovered from it by further processing.

Another approach to energy savings would be to reduce the 45 percent of process metal that is recirculated. This would



increase the pounds shipped per pound melted, reducing energy consumption in both remelt operations as well as the melting loss.

Since the energy crisis, most fabrication and finishing shops throughout the world have found they can achieve significant energy reductions (and, therefore, also cost reductions) in their operations. Savings of 10-25 percent in energy consumed are not uncommon, with the savings coming from a variety of factors, examples being the following:

1. replacement of direct fired furnaces by  
radiant tube furnaces,
2. improved furnaces and insulation,
3. improved scheduling,
4. replacement of gasoline trucks by  
electric trucks,
5. general plant maintenance and personnel  
education programs,
6. scrap reduction programs.

#### Recycling of "New" Scrap

Essentially all "new" aluminum scrap is recycled. This is scrap generated by primary producers, fabricators, and manufacturers of industrial or consumer products. Whenever possible the metal is kept segregated as to alloy and reprocessed by primary or secondary smelters.

Once the aluminum metal is received at the primary or secondary smelter (preferably segregated as to alloy), it is melted. The minimum energy thermodynamically required to melt a kilogram of aluminum is about 1100 BTU's whereas about 7000 BTU's are actually used. Thus, improving melting efficiency is possible and desirable. Probably greater potential for energy savings lies in learning to melt scrap with less oxidation losses. Technologies known in the trade to reduce these losses include minimizing fires, melting with salt additions or in deep salt baths, and removing oil and coatings prior to melting. Better methods are needed.

Of course, oxidation of aluminum occurs with each melting. In North America, approximately 550,000 tons of dross containing 70 percent free metal are generated per year. Of this 390,000 tons of metal, not more than half is ultimately recovered. The total resulting loss of aluminum (from oxidation of the metals, and un-recovered in the dross) is 270,000 tons, worth about 150 million dollars. A number of different processes are used today to recover the metal but improved, less polluting, processes are needed.

#### Recycling "Old" Scrap

A major opportunity for energy and materials savings lies in the area of recycling "old" scrap (i.e., scrap from discarded, used, worn, worn out products). In a Battelle study conducted



for the year 1969 in the United States, it was estimated that only some 13.1 percent or 159,000 tons of the aluminum that was becoming obsolete was actually recycled. Thus the aluminum (i.e., the "old" scrap) not being recycled was approximately one million tons, Table 6. The study also indicated that by 1979 the estimated aluminum not recycled would be 4.8 million tons, Table 7. The industry sources indicate the actual amount of aluminum being discarded may already be substantially higher than this 4.8 million tons.

Some substantial success is now being achieved with recycling of one specific product (aluminum cans) and significant gains would seem to be feasible for other products (automobiles, home appliances). The recycling of aluminum cans started in 1967 on a "charity" basis. By 1968, 22¢/Kg was being paid for incentive. The industry is now paying 33¢/Kg. Currently, there are 1300 recycle centers in the United States which handled 1.6 billion cans, or 16 percent of production in 1973, Table 8. Special processing is required because of dirt, paint and coatings on used cans. Some processors shred and redensify, others do not. Special melting facilities are required.

Other than aluminum cans, the only full scale recovery operation of non-industrial aluminum waste currently in existence is that of auto bodies. The bodies are shredded, aluminum segregated by one of several methods and then remelted and alloyed to a die casting specification. Some limited purification may also be employed.

TABLE 6  
OLD ALUMINUM SCRAP RECYCLING, 1969

THOUSANDS OF METRIC TONS

<u>Scrap Source</u>	<u>Estimated Aluminum Becoming Obsolete</u>	<u>Estimated Old Aluminum Recycled</u>	<u>Estimated Percent Recycled</u>	<u>Estimated Aluminum Not Recycled</u>
Building and Construction	65.0	8.2	13.0	56.4
Transportation	299.0	90.9	30.0	208.2
Consumer Durables	179.0	22.7	13.0	156.4
Electrical	6.4	5.9	93.0	.5
Machinery and Equipment	55.0	13.6	25.0	41.8
Containers and Packaging	442.0	1.8	0.4	440.0
Other	<u>166.0</u>	<u>15.9</u>	<u>9.2</u>	<u>150.4</u>
TOTALS	1,212.0	159.0	13.1	1,054.0

Source: "A Study to Identify Opportunities for Increased Solid Waste Utilization," Battelle, Columbus Laboratories, June, 1972.

TABLE 7  
OLD ALUMINUM SCRAP RECYCLING, 1969-1979  
THOUSANDS OF METRIC TONS

<u>Year</u>	<u>Estimated Aluminum Becoming Obsolete</u>	<u>Estimated Old Aluminum Recycled</u>	<u>Estimated Percent Recycled</u>	<u>Estimated Aluminum Not Recycled</u>
1969	1212.7	159	13.1	1054
1974	1791.0	295	16.5	1497
1979	2717.3	410	15.1	2307

Source: "A Study to Identify Opportunities for Increased Solid Waste Utilization," Battelle, Columbus Laboratories, June, 1972.

TABLE 8  
ALUMINUM CAN RECYCLING PROGRAM 1968-74

Year	<u>Returned to Aluminum Industry Number Cans<sup>1</sup></u>	<u>Payments<sup>2</sup></u>	<u>Aluminum Cans Produced<sup>3</sup></u>	<u>Percent Returned</u>
1968	-----	\$ -----	1.7 billion	----
1969	-----	-----	2.7 billion	----
1970	185 million	800,000	3.7 billion	5
1971	770 million	3.4 million	6.2 billion	12
1972	1.2 billion	5.2 million	8.4 billion	14
1973	1.6 billion	7.0 million	10.6 billion	15
1974	2.3 billion	-----	13.9 billion	----

<sup>1</sup>Aluminum cans run 23 per pound in 12-ounce size. Figures are based on metal equivalent of 12-ounce cans.

<sup>2</sup>Prior to June 1, 1974, price was \$.10/lb., after June 1, 1974, price was \$.15/lb.

<sup>3</sup>Includes 7-ounce, 10-ounce, 11-ounce, 12-ounce and 16-ounce cans.

Data Provided by Reynolds Metals Company Market Research Department

Another potential use for the automobile shredder would be in the area of shredding white goods; that is, stoves, refrigerators, washers and the like, which are discarded in large quantities every year. The United States National Industrial Pollution Control Council estimated that over 64,000 metric tons of aluminum could be available in 1974 if appliance discards were all recycled. These products all contain substantial quantities of zinc, copper and steel, in addition to the aluminum. Processing to recover these metals can add additional large quantities of metals to the national economy.

#### Recycling Aluminum from Municipal Waste

Table 9 gives the composition of municipal waste found in the United States. This table indicates that the metal content of municipal waste, which is of interest to those attending here today, shows 6.7 percent ferrous metals, 0.9 percent aluminum and 0.4 percent heavy nonferrous metals. This table is very significant since in the United States today we generate somewhere around 125 million metric tons of municipal waste annually. The amount of aluminum present, as determined by the National Center for Resource Recovery on the basis of input analysis, less current recycling, is three-quarters of a million metric tons, or over 10 percent of the total annual aluminum shipment in the United States in 1973. Output analysis, based on analysis of actual refuse samplings, indicates a nationwide average of 0.8 percent aluminum in

TABLE 9

COMPOSITION OF MUNICIPAL SOLID WASTE IN THE UNITED STATES<sup>1</sup>

Paper	42.7%	Back Yard Waste	12.5%
Glass	10.3	Plastics	1.7
Ferrous	6.7	Textile	2.4
Aluminum	0.9	Wood	2.5
Heavy Non-ferrous	0.4	Leather & Rubber	1.8
Food	14.6	Miscellaneous	4.5

---

<sup>1</sup>National Center for Resource Recovery average of 24 surveys taken in various communities. Total comes to more than 100% due to rounding off of individual items.

the waste, or a total of one million metric tons per year potentially available from this one source. Obviously, this amount of aluminum, as well as the other nonferrous metals present, represents a substantial addition to the sources of metal that the metal fabricating industry now uses and will so sorely need in the years to come.

The collection and recycling of this municipal waste is a problem that is under study in most developed nations. Projects under way in the United States include a municipal plant being built in New Orleans with the assistance of the Federal Government and a multi-industry research and development group, to recover aluminum and glass from solid waste, and to provide landfill. A second project, sponsored by the government and industry is studying the effectiveness of a so called "aluminum magnet" (an eddy current device) for separating aluminum from other metals.

Without going into great detail, three systems for processing municipal waste are illustrated by the diagrams of Tables 10, 11 and 12. Table 10 shows a typical "front end" separation method in which waste is separated into various subsystems or side streams, which are then ready for direct recycling or can be further treated.

A typical "back end" system is shown in Table 11, in which incineration is first conducted, and separation of metallic

TABLE 10

GENERAL RESOURCE RECOVERY PROCESS FOR MMR

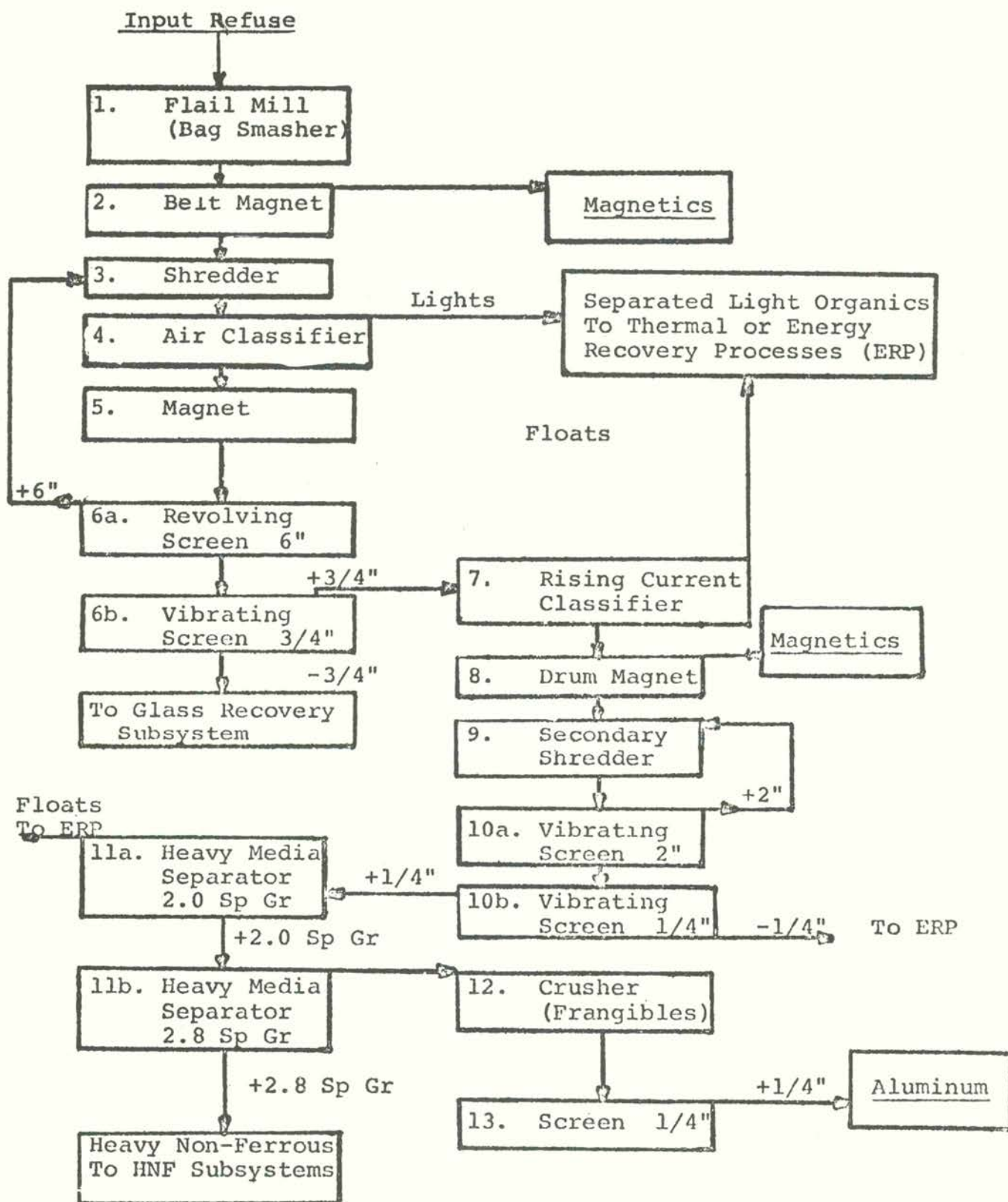




TABLE 11  
 U. S. BUREAU OF MINES  
 INCINERATOR RESIDUE PILOT PLANT PROCESS FLOW SHEET

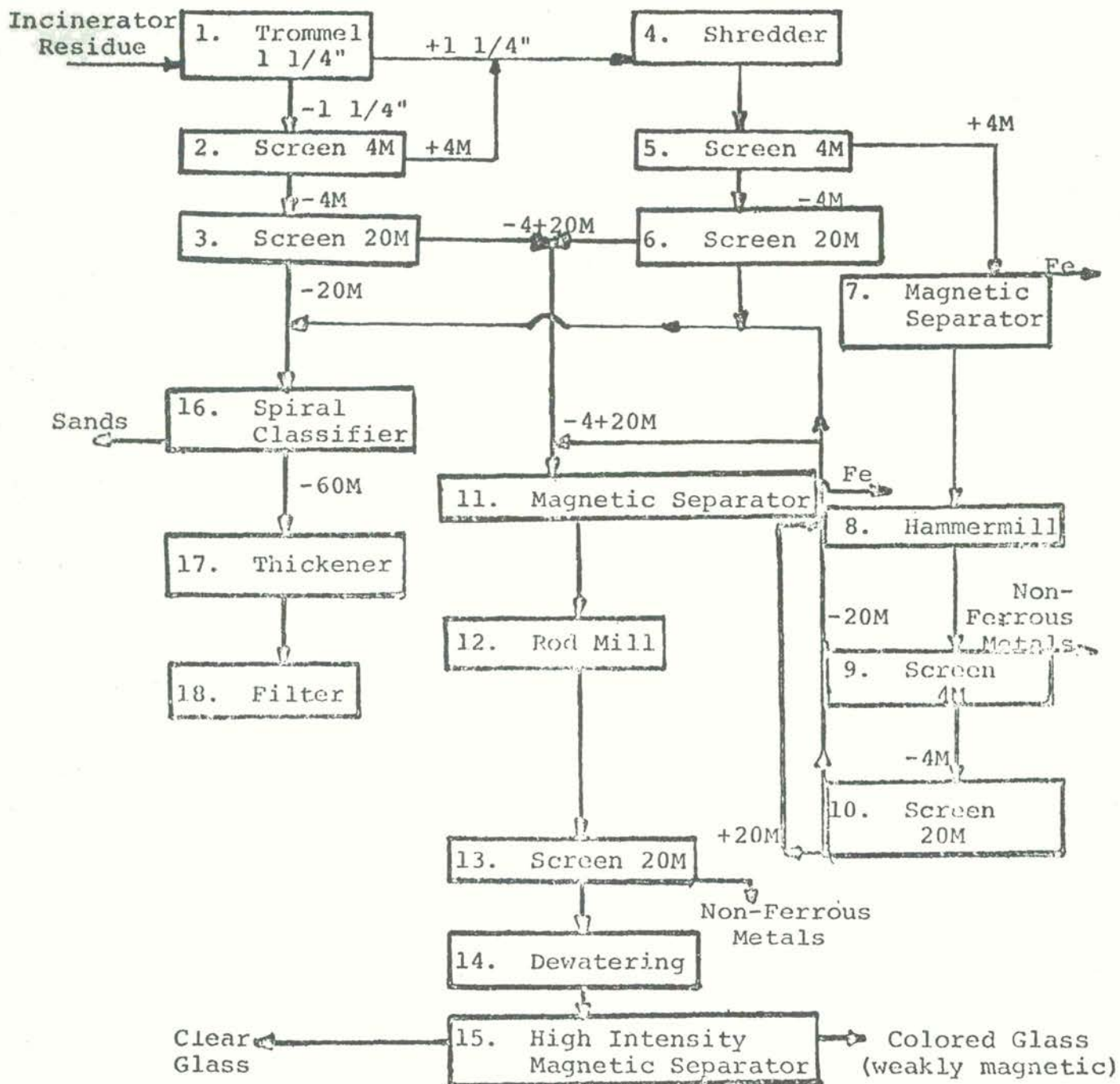
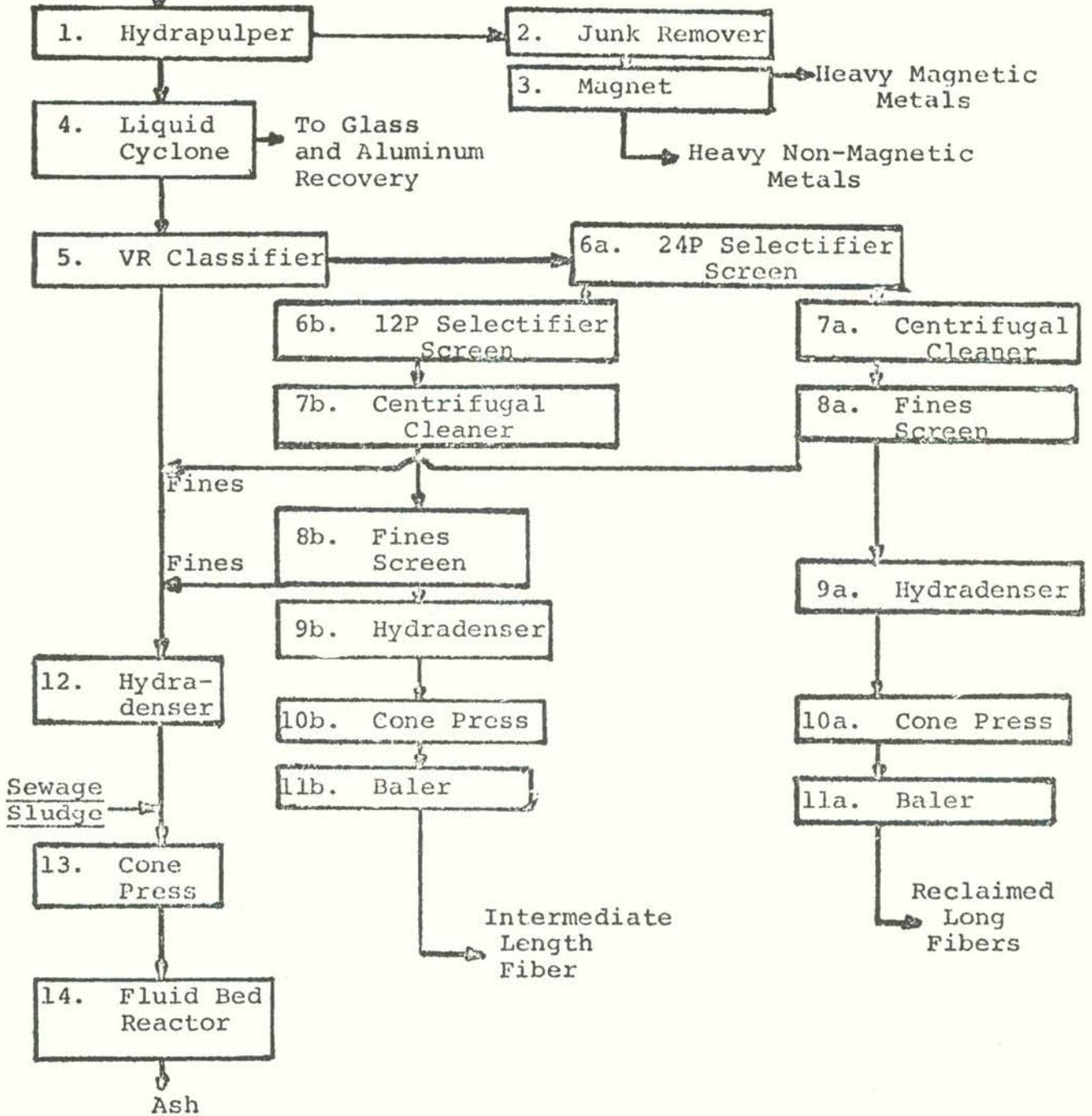


TABLE 12

BLACK CLAWSON CO. - RECLAMATION SYSTEM FLOW DIAGRAM  
FRANKLIN, OHIO

Mixed Municipal Refuse



constituents is done in later steps. A variation of the "front end" system is the "hydrapulping" process of Black and Clawson, Table 12.

Preliminary studies have indicated that aluminum metal recovered from both the "front end" and "back end" separation processes is usable in either manufacture of wrought or cast products.



**UNITED NATIONS  
ENVIRONMENT PROGRAMME**



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Aluminium Meeting

Paris, 6-8 October 1975

STANDARDS RELEVANT TO  
THE ALUMINIUM INDUSTRY

Note : For the information of delegates to the Seminar, the Secretariat has prepared a list of standards relevant to the Aluminium Industry as follows :

- I. Air Quality Standards
- II. Standards for Fluorides in Forage
- III. Emission Standards

It should be noted that this list is not necessarily fully inclusive or completely up to date.

FLUORIDES AIR QUALITY STANDARDS ( all countries except U.S. )

Fluorides (as F)	Bulgaria	<u>0.02</u>	0.01	24 hr	<u>0.005</u>	0.002	20 min.	
Fluorides (as F)	Canada Ontario	0.001	<u>0.0005</u>	30 days	-	-	-	desirable air quality
Fluorides (as F)	Canada Ontario	0.002	<u>0.001</u>	24 hr	-	-	-	desirable air quality
Fluorides (as F)	Czechoslovakia	<u>0.01</u>	0.005	24 hr	<u>0.03</u>	0.015	30 min	HS, Si F <sub>4</sub>
Fluorides (as F)	East Germany	<u>0.005</u>	0.002	24 hr	<u>0.02</u>	0.01	30 min	HS, Si F <sub>4</sub>
Fluorides (as F)	Hungary	<u>0.03</u>	0.015	24 hr	<u>0.1</u>	0.05	30 min	
Fluorides (as F)	Hungary	<u>0.01</u>	0.005	24 hr	<u>0.03</u>	0.015	30 min	highly protected and protected areas
Fluorides (as F)	Israel	0.01	<u>0.005</u>	24 hr	0.03	<u>0.015</u>	30 min	tentative standard
Fluorides (as F)	Italy	<u>0.02</u>	0.01	24 hr	<u>0.06</u>	0.03	30 min	not to be exceeded more than once in 8 hours
Fluorides (as F)	Romania	<u>0.005</u>	0.002	24 hr	<u>0.02</u>	0.01	30 min	
Fluorides (as F)	Spain	<u>0.02</u>	0.01	24 hr	<u>0.06</u>	0.03	30 min	proposed
Fluorides (as F, gaseous compounds)	USSR	<u>0.005</u>	0.002	24 hr	<u>0.02</u>	0.01	20 min	see Table 1
Fluorides (gaseous and salt combined)	East Germany	<u>0.01</u>	-	24 hr	<u>0.03</u>	-	30 min	
Fluorides (as HF)	Canada Manitoba	<u>0.0015</u>	<u>0.002</u>	24 hr	-	-	-	Max. acceptable level
Fluorides (as HF)	Canada Manitoba	<u>0.0008</u>	<u>0.0006</u>	24 hr	-	-	-	desirable level
Fluorides (as HF)	Canada New Found-land	<u>0.00045</u>	<u>0.005</u>	30 days	<u>0.0009</u>	<u>0.001</u>	24 hr	
Fluorides (as HF)	Canada Saskatchewan	<u>0.003</u>	<u>0.004</u>	24 hr	-	-	-	provisional maximum

fluorides (as HF)	Hungary	<u>0.02</u>	0.015	24 hr	0.015	30 min	
fluorides (as HF)	Hungary	<u>0.0013</u>	0.001	24 hr	<u>0.005</u>	0.004	highly protected & protected areas
fluorides (as HF)	Netherlands	<u>0.01</u>	0.008	24 hr	-	-	
fluorides (as HF)	Spain	<u>0.01</u>	0.008	24 hr	<u>0.03</u>	0.022	proposed
fluorides (as HF)	USSR	<u>0.01</u>	0.008	24 hr	<u>0.03</u>	0.022	NaF, Na <sub>2</sub> SiF <sub>6</sub> , see Table 1
fluorides (as HF)	West Germany	<u>0.002</u>	0.015	30 min	<u>0.005</u>	0.004	30 min
fluorides (as HF)	Yugoslavia	<u>0.005</u>	0.004	24 hr	<u>0.02</u>	0.015	30 min
fluorides (readily soluble inorganic)	Bulgaria	<u>0.01</u>	-	24 hr	<u>0.03</u>	-	20 min NaF, Na <sub>2</sub> SiF <sub>6</sub>
fluorides (readily soluble inorganic)	East Germany	<u>0.01</u>	-	24 hr	<u>0.03</u>	-	30 min NaF, Na <sub>2</sub> SiF <sub>6</sub>
fluorides (readily soluble inorganic)	Poland	<u>0.01</u>	-	24 hr	<u>0.03</u>	-	1 20 min for protection areas
fluorides (readily soluble inorganic)	Poland	<u>0.003</u>	-	24 hr	<u>0.01</u>	-	20 min special protection areas
fluorides (readily soluble inorganic)	Yugoslavia	<u>0.01</u>	-	24 hr	<u>0.03</u>	-	30 min NaF, Na <sub>2</sub> SiF <sub>6</sub>
fluorides (sparingly soluble)	East Germany	<u>0.03</u>	-	24 hr	<u>0.2</u>	-	30 min AlF <sub>3</sub> , NaAlF <sub>6</sub> , CaF <sub>2</sub>
fluorides (sparingly soluble)	USSR	<u>0.03</u>	-	24 hr	<u>0.2</u>	-	30 min AlF <sub>3</sub> , NaAlF <sub>6</sub> , CaF <sub>2</sub> see Table 1
fluorides (in mixture with gaseous)	Bulgaria	<u>0.01</u>	-	24 hr	<u>0.03</u>	-	30 min
fluorides (insoluble)	Yugoslavia	<u>0.03</u>	-	24 hr	<u>0.2</u>	-	30 min

A. If several substances with synergistic toxic properties are present in the air, the maximum permissible concentration (MPC) of the mixture is calculated from the following formula:

$$X = \frac{A}{M_1} + \frac{B}{M_2} + \frac{C}{M_3} \quad (1)$$

where X is the (relative) MPC; A, B, C, are the concentrations of the substances in the mixture and  $M_1$ ,  $M_2$ ,  $M_3$ , their respective maximum permissible concentrations.

B. If formula (1) is applied to the following two, three or four component systems, the value X: should not exceed 1.0 for

- |                                               |                                                                                                            |
|-----------------------------------------------|------------------------------------------------------------------------------------------------------------|
| (a) acetone and phenol                        | (f) H <sub>2</sub> S and "dinyll"                                                                          |
| (b) SO <sub>2</sub> and phenol                | (g) isopropyl benzene and isopropyl benzene hydroperoxide                                                  |
| (c) SO <sub>2</sub> and NO <sub>2</sub>       | (h) furfural, methanol, and ethanol                                                                        |
| (d) SO <sub>2</sub> and HF                    | (i) strong mineral acids (sulfuric, hydrochloric, and nitric, concentrations expressed as H <sup>+</sup> ) |
| (e) SO <sub>2</sub> and sulfuric acid aerosol | (j) ethylene, propylene, butylene and anylene                                                              |

should not exceed 1.3 for

acetic acid and acetic anhydride

should not exceed 1.5 for

- (a) acetone and acetophenone
- (b) benzene and acetophenone
- (c) phenol and acetophenone

C. If (a) H<sub>2</sub>S and CS<sub>2</sub>, (b) CO and SO<sub>2</sub>, (c) phthalic anhydride, maleic anhydride and  $\alpha$ -naphthoquinone are present in the mixture, the MPC values of individual substances should not be exceeded.

D. If p-chlorophenyl isocyanate is present together with m-chlorophenyl isocyanate the MPC is determined by the presence of the more toxic substance i.e., of p-chlorophenyl isocyanate.

FLUORIDES AIR QUALITY STANDARDS ( U.S. )

Fluorides	Kentucky	0.00032 0.00164 0.00286 0.00368	1 month. 7 days 24 hrs. 12 hrs.	) ) ) )	as hydrogen fluoride
Fluorides	Kentucky	0.04 0.06 0.08	growing season 2 months 1 month	) ) )	
	Jefferson Co.				
Fluorides	New Hampshire	0.04 0.06 0.08 0.001 0.002 0.0035 0.0045	1 month 2 months 1 month 1 month 7 days 24 hrs. 12 hrs.	) ) ) ) ) ) )	total fluorides, during growing season total fluorides' total fluorides, for the whole year as hydrogen fluorides
Fluorides	Pennsylvania	0.005	7 days	)	
Fluorides	South Carolina	0.3µS/ cm <sup>2</sup> /mo	30 days	)	
Fluorides	Tennessee	0.0012 0.0016 0.0029 0.0037	1 month 7 days 24 hrs. 12 hrs.	) ) ) )	as hydrogen fluorides
Fluorides	Washington	0.0034 0.0017 0.0029 0.0037	1 month 7 days 24 hrs. 12 hrs.	) ) ) )	



FLUORIDES IN FORAGE STANDARDS OTHER THAN  
THOSE FROM SUBSIDIARY JURISDICTION OF THE UNITED STATES

<u>Country</u>	<u>Province</u>	<u>Standard</u>
Canada	Newfoundland	35 ppm (by wt.) individual sample
	Manitoba	35 ppm individual sample
	Ontario	35 ppm
	Manitoba	40 ug/100 cm <sup>2</sup> (30 days)
	Ontario	40 ug/100 cm <sup>2</sup> (30 days)

FLUORIDES IN FORAGE STANDARDS

OF THE UNITED STATES

State	Standard (ppm)	Averaging Time
Idaho	40.0	Annual Arithmetic Mean
	60.0	30 days (for 2 consec. months)
	80.0	30 days - 100%
Kentucky	40.0	30 days (for 6 consec. months)
	60.0	2 months
	80.0	1 month 100%
Montana	35.0	peak
	0.3 µg/cm <sup>3</sup>	28 days
Texas	40.0	1 yr.
	60.0	30 days (for 3 consec. months)
Washington	80.0	30 days (for 2 consec. months)
	40.0	1 yr.
	60.0	2 consec. months
	80.0	1 month

EMISSION STANDARDS FOR ALUMINIUM PLANTS ( all countries except U.S.)

<u>Gases</u>		<u>orig. units</u>	<u>mg/m<sup>3</sup></u>	<u>remarks</u>
Chlorine	Australia Victoria	0.1 grain/ft <sup>3</sup>	228.8	STP : 0°C, 1 atm.
Chlorine	Czechoslovakia	1.0 kg/hr		if above reporting required
Chlorine	Singapore	0.2 g/m <sup>3</sup>	200.0	
Chlorine	West Germany	Aluminium reduction	3.0	
Fluorine	Australia N.S. Wales	Aluminium reduction	20.0	as hydrofluoric acid
Fluorine	Australia N.S. Wales	any other process	50.0	as hydrofluoric acid
Fluorine	Australia Queensland	any industry	114.4	as hydrofluoric acid
Fluorine	Australia Victoria	manufacturing of aluminium	50.0	as hydrofluoric acid
Fluorine	Czechoslovakia	gaseous in organic compound	0.3 kg/hr	
Fluorine	Japan	Aluminium reduction discharge duct	3.0	
Fluorine	Japan	Aluminium reduction roof vents	1.0	
Fluorine	Singapore	any source	100.0	
Fluorine	West Germany (VO 1 2286)	Aluminium reduction	50.0	
Fluorine compounds	Australia	Aluminium reduction	20.0	proposed national
Fluorine in organic comp.	Australia N.S. Wales	Aluminium reduction	20.0	
Fluorine in organic comp.	Australia Queensland	Aluminium reduction	50.0	

\* Note these emission standards are not additive for a particular country

<u>Gases</u>		<u>orig. units</u>	<u>mg/m<sup>3</sup></u>	<u>remarks</u>
Fluorine in organix comp.	Australia Victoria	0.05 grain/ft <sup>3</sup>	114.4	manufacturing aluminium
Hydrogen fluoride	Japan	mg/m <sup>3</sup>	3.0	Aluminium reduction discharge ducts
Hydrogen fluoride	Japan	mg/m <sup>3</sup>	1.0	Aluminium reduction roof vents
Hydrogen fluoride	West Germany	mg/m <sup>3</sup>	2.0	Aluminium reduction
Hydrogen fluoride	West Germany	1 kg/ton Al		Aluminium reduction closed furnaces
Hydrogen fluoride	West Germany	0.8 kg/ton Al		Aluminium reduction open furnaces
Silicon fluoride	Japan	mg/m <sup>3</sup>	3.0	Aluminium reduction discharge ducts
Silicon fluoride	Japan	mg/m <sup>3</sup>	1.0	Aluminium reduction roof vents
<u>Suspended Particulates</u>				
Metal Heating	Australia	0.1 g/m <sup>3</sup>	100.0	guidelines
Metal Heating	Australia Queensland	0.05 grains/ft <sup>3</sup>	114.0	
Metal Heating	Australia Victoria	0.10 grains/ft <sup>3</sup>	114.0	
Metal Heating	Japan			
40,000 m <sup>3</sup> /hr gas	special district	0.2 g/m <sup>3</sup>	200.0	
40,000 m <sup>3</sup> /hr gas	other districts	0.4 g/m <sup>3</sup>	400.0	

<u>Suspended Particulates</u>		<u>orig. units</u>	<u>mg/m<sup>3</sup></u>	<u>remarks</u>
Metal Heating	Japan (cont'd)			
40,000 m <sup>3</sup> /hr gas	special district	0.1 g/m <sup>3</sup>	100.0	
40,000 m <sup>3</sup> /hr gas	other districts	0.2 g/m <sup>3</sup>	200.0	
Processes				
Alloy Production	West Germany	mg/m <sup>3</sup>	75.0	
Alumina Calcination	West Germany (VO1 2286)	mg/m <sup>3</sup>	100.0	
Alumina grinding	West Germany (VO1 2286)	mg/m <sup>3</sup>	150.0	
Close furnace	West Germany	12 kg/ton Al		
Open furnace	West Germany	14 kg/ton Al		
primary reduction	West Germany	mg/m <sup>3</sup>	75.0	
secondary recovery rotary furnace	West Germany (VO1 2241)	1% of production		
secondary recovery other furnace	West Germany (VO1 2241)	0.3 g/m <sup>3</sup>	300.0	
Smelter	Great Britain	0.05 grains/ft <sup>3</sup>	114.4	fume emission from use of salt as a flux

no standards on national level

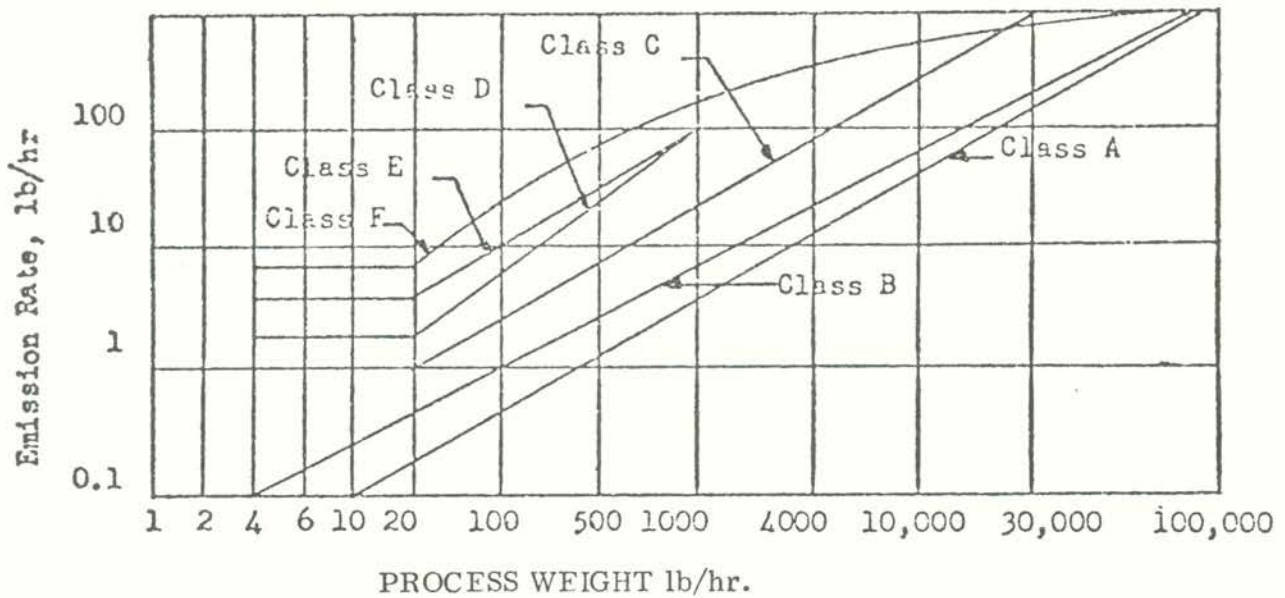
Gases

Chlorine	Any source	Connecticut	Norwalk	---	see Fig. 1
Chlorine	Any source	Connecticut	Stamford	---	see Fig. 1
Fluorine	Any source	Idaho, New Hampshire Washington	---	---	shall not cause Air Quality for Forage Standard to be exceeded
Fluorine	Any source	Florida	Manatee Co.	0.2 lb/tonP <sub>2</sub> O <sub>5</sub>	---
Fluorine	Any source	Georgia	Yacon-Bibb Co.	0.4 lb/tonP <sub>2</sub> O <sub>5</sub>	---
Fluorine	Any source	Mississippi	---	0.4 lb/tonP <sub>2</sub> O <sub>5</sub>	---
Fluorine	Any source	Texas	---	---	shall not cause Air Quality for Forage Standard to be exceeded
Fluorine	Built before 1/1/72	Georgia	---	0.4 lb/tonP <sub>2</sub> O <sub>5</sub>	---
Fluorine	Built after 1/1/72	Georgia	---	0.2 lb/tonP <sub>2</sub> O <sub>5</sub>	---
Fluorine	Built before 4/4/73	Georgia	Fulton Co.	0.4 lb/tonP <sub>2</sub> O <sub>5</sub>	---
Fluorine	Built after 4/4/73	Georgia	Fulton Co.	0.2 lb/tonP <sub>2</sub> O <sub>5</sub>	---
Fluorine	New source	Florida	Orange Co.	0.4 lb/tonP <sub>2</sub> O <sub>5</sub>	---
Fluorine	Primary aluminum				
Fluorine	> 200Mtons/yr	Montana	---	0.06 lb/hr/CaII	---

For gases, the following standards shall apply.

The Director of Health shall determine the class of any particular gas.

AVERAGE EMISSION - RATE POTENTIAL lb/hr.



Class	Gases*
A	Nickel carbonyl
B	Phosphine
C	Acrolein, bromine, fluorine
D	Chlorine, HCHO, HCl, SO <sub>2</sub>
E	Alkyl alcohol, HB, HCN, NO <sub>2</sub> , H <sub>2</sub> S
F	Acetic acid, NH <sub>3</sub> , methyl acrylate

\* Examples only. Not all inclusive

Each curve gives the allowable emission rates for each class of gases in terms of the rate at which the gases would be emitted ( potential rate of pollutant emission) in the absence of gas cleaning devices.

Figure 1 - Regulating the Rate of Emission of Gaseous Pollutants the Atmosphere - Norwalk and Stamford , Connecticut

SUSPENDED PARTICULATESStandard      Remarks

Primary aluminum mfg.

Euilt before 1/1/73	Oregon	13 lb/ton Al	monthly average
Euilt before 1/1/73	Oregon	10 lb/ton Al	annual average
Euilt after 1/1/73	Oregon	7 lb/ton Al	monthly average
Euilt after 1/1/73	Oregon	5 lb/ton Al	annual average
Horizontal stud Soderberg	Louisiana	12 lb/ton Al	
Prebake process	Louisiana	10 lb/ton Al	
Solid particulate matter	Alabama	15 lb/ton Al	per ton produced, daily basi
Solid particulate matter	Washington	15 lb/ton Al	per ton produced, daily basi
Total particulate matter	Alabama	22 lb/ton Al	per ton produced, daily basi

Secondary aluminum  
manufacturing

see Table 2

Melting and Refining

see Table 2

Sweating



Table 2 - Particulate Emission

Pennsylvania

$$A = 0.76E^{0.42}$$

where:

A = Allowable emissions in pounds per hour<sup>a</sup>.

E = Emission index = F x W pounds per hour.

F = Process factor in pounds per unit, and

W = Production or charging rate in units per hour.

Process

Process Factor, F (in pounds per ton)

Carbon Black manufacturing	500 (product)
Charcoal manufacturing	400 (product)
Crushers, grinders, or screens	20 (feed)
Paint manufacturing	0.05 (pigment handled)
Phosphoric acid manufacturing	6.0 (phosphorous burned)
Detergent drying	30 (product)
Alfalfa dehydration	30 (product)
Grain elevators (loading and unloading)	90 (grain)
Grain screening and cleaning	300 (grain)
Grain drying	200 (product)
Meat smoking	0.01 (meat)
Ammonium nitrate manufacturing (granulator)	0.1 (product)
Ferroalloy production furnace	0.3 (product)
Primary iron and/or steel making:	
Iron production	100 (product)
Sintering - windbox	20 (dry solids feed)
Steel production	40 (product)
Scarfing	20 (product)
Primary lead production:	
Roasting	0.004 (ore feed)
Sintering - Windbox	0.2 (sinter)
Lead reduction	0.5 (product)
Primary zinc production:	
Roasting	3 (ore feed)
Sintering - windbox	2 (product)
Zinc reduction	10 (product)

Table 2 - (continued) Particulate Emission

## Pennsylvania

Secondary aluminum production:	
Sweating	50 (aluminum product)
Melting and refining	10 (aluminum feed)
Brass and bronze production (melting and refining)	20 (product)
Iron foundry:	
Melting:	
Five tons per hour and less	150 (iron)
More than five tons per hour	50 (iron)
Sand handling	20 (sand)
Shake-out	20 (sand)
Secondary lead smelting	0.5 (product)
Secondary magnesium smelting	0.2 (product)
Secondary Zinc smelting:	
Sweating	0.01 (product)
Refining	0.3 (product)
Asphaltic concrete production	6 (aggregate feed)
Asphalt roofing manufacturing: (felt saturation)	0.6 (asphalt used)
Portland cement manufacturing:	
Clinker production	150 (dry solids feed)
Clinker cooling	50 (product)
Coal drying	2 (product)
Coal dry-cleaning	2 (product)
Lime calcining	200 (product)
Petroleum refining (catalytic cracking)	40 (liquid feed)



**UNITED NATIONS  
ENVIRONMENT PROGRAMME**



**FLUORIDE AND PLANT LIFE**

**Leonard H. Weinstein  
Boyce Thompson Institute for Plant Research  
1086 North Broadway  
Yonkers, New York 10701**

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## FLUORIDE AND PLANT LIFE

### Introduction

Effects of fluoride on agriculture were first recorded in the Icelandic literature about 1000 years ago as a result of volcanic eruptions. Livestock that ate grass contaminated with the fallen ash became sick and exhibited symptoms now associated with acute and chronic fluoride toxicity or fluorosis. The symptoms disappeared when the animals were taken indoors and fed on hay mown before the eruptions (Roholm, 1937). It was many years before the problem was understood.

Near the end of the 19th century, there were two significant occurrences. First, the element fluorine was isolated by Moissan (1900). Second, Mayrhofer (1893), Rhode (1895), Wislicenus (1898), and Ost (1907) described fluoride-induced injury to plants in the vicinity of superphosphate plants, brick works, and glass factories. It was not until the reports of Wilczek (1916) and Faes (1921) that fluoride injury to crops as a result of alumina reduction was first reported in Europe, and 1946 before it was reported in the U.S. (de Ong, 1946). But the potential for injury by industrial effluents was present much earlier because fluoride-containing minerals, such as fluorspar ( $\text{CaF}_2$ ), have been used as metallurgical fluxes since at least the end of the 15th century and, mixed with sulfuric acid, for etching glass since the 17th century (Eméleus, 1950).

The purpose of this review is to summarize the state of our knowledge with respect to the known impacts of fluorine-containing compounds from alumina reduction smelters on cultivated and indigenous vegetation, their transfer in the environment, and the abiotic and biotic factors that affect the response of plants to the pollutants. But the scope of the review will be limited only to the effects of alumina reduction plants independent of the means of power generation used to supply them. Thus, the environmental problems posed by coal-burning power generating plants which emit sulfur oxides, nitrogen oxides, fluorides, fly ash, etc., by their thermal discharges or the means used to cool these discharges, such

as cooling towers (with their emissions of moisture and salts), will not be addressed. When air pollutants are ranked in importance with respect to plant damage in the U.S., fluoride is ranked third, after ozone and sulfur dioxide. But fluoride is the most phytotoxic of the important pollutants, with the potential of causing injury to susceptible plant species at atmospheric concentrations well below 1 part per billion. By contrast, ozone and sulfur dioxide concentrations must be about 100-fold greater to cause injury to plants. Fluoride has one other unique characteristic: it is accumulative.

#### The Functions of Plants in the Environment

Any plant or population of plants may serve three different functions: commercial, aesthetic, or ecologic. Among the commercial functions are agriculture and forestry, in which the plants are the basis for the production of food, forage, fiber, and fuel. The aesthetic functions are exemplified by private gardens and public parks. The most complex of these functions is the ecologic because it includes oxygen production, provision of habitats and food for wildlife, roles in soil and water conservation, and the recycling of nutrients. These functions can be satisfied by any plant or plant community, or specific plants can be grown on the basis of their suitability to a desired function. The effect of atmospheric fluoride on a plant becomes significant when this effect is related to one of these plant functions, and the degree of its significance will depend upon the probability of its occurrence and the ability to extrapolate the commercial, aesthetic, or ecologic impacts of this effect.

#### Transfer of Fluoride in the Environment

A summary of the transfer of fluoride in the environment is shown in Figure 1, where the various routes by which fluoride passes to and from the atmosphere, hydrosphere (the earth's waters), lithosphere (the earth's crust), and biosphere (living organisms) are illustrated. The known pathways due both

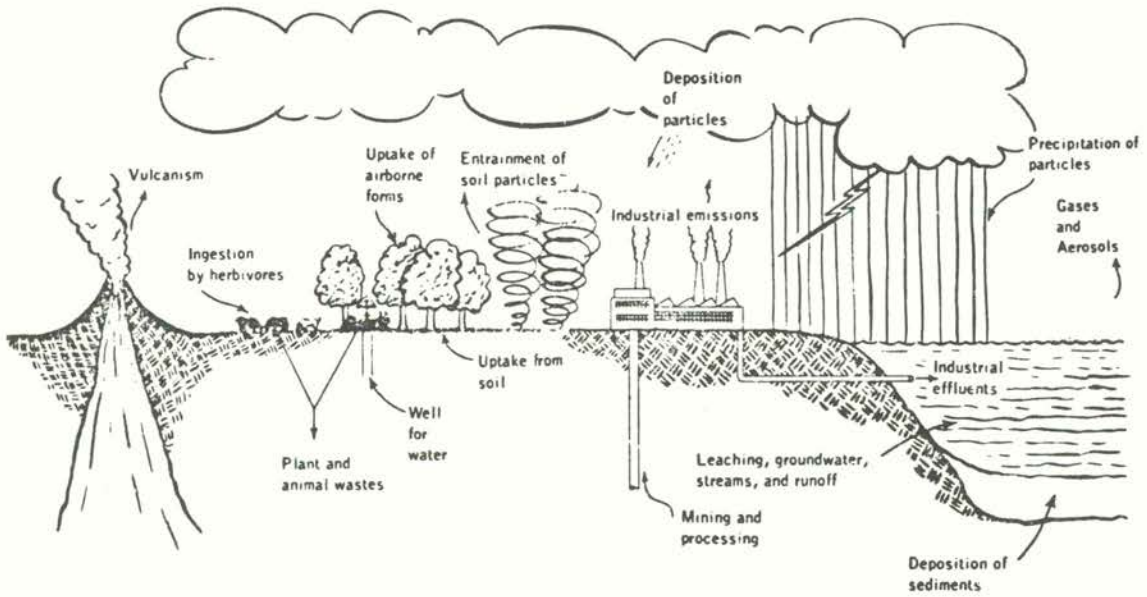


Figure 1. Environmental transfer of fluoride (FLUORIDES, 1971).

to natural phenomena or to man's activities are shown.

Vulcanism and the entrainment of soil particles are the natural routes by which gaseous and particulate fluorides pass from the earth's crust to the atmosphere; vaporization and aerosol formation are possible routes from the waters. Atmospheric fluoride returns to the waters or earth's crust by deposition of particulate materials or through precipitation. The transfer of fluoride from the earth's crust to its waters can occur through the leaching of minerals or the addition of particulate matter to groundwater and streams. The return route would be by the deposition of sediments. The terrestrial portion of the biosphere is an intermediate stage in the passage of atmospheric fluoride to the earth's crust. Fluoride accumulated by vegetation can pass to the soil through plant wastes or enter the food chain through herbivores and ultimately through animal wastes. When fluoride is taken up by vegetation from the soil solution, its passage through the living organisms represents a recycling of fluoride from other sources.

When industrial and other human activities are superimposed on the natural transfer mechanisms of fluoride, they result in new routes of transfer and an increased flow through pre-existing ones. For example, the emission of particulate and gaseous fluorides in the reduction of alumina represents a path from the earth's crust to the atmosphere. Its removal is by natural means. The inhalation of fluoride by man and animals is another route into the biosphere, but is of concern only in industrial atmospheres. Similarly, the passage of fluoride derived from the earth's crust to the hydrosphere in industrial effluents and waste water will increase the fluoride burden in the aquatic environment and subsequent flow by natural routes to other parts of the environment.

There are no quantitative estimates of the amount of fluoride partitioned into the different phases of the environment, its residence times, or its rate of transfer. But a gross estimate of two pathways into the atmosphere can be obtained.

About 30 million tons of soil are distributed into the atmosphere each year in the United States; with a mean fluoride concentration of 190 ppm in soil, this implies about 6,000 tons of fluoride. Total emissions from all industrial processes and for primary aluminum production in the United States for 1968 were estimated at 119,000 tons and 16,000 tons, respectively (FLUORIDES, 1971).

#### Organic Transformation of Fluoride

More than two dozen plant species are known to convert fluoride obtained from soil or soil water into carbon-fluorine compounds that have a much greater mammalian toxicity than the inorganic fluoride from which they derived.

In 1944, the presence of monofluoroacetic acid was reported to occur in the South African plant, Dichapetalum cymosum, or gifblaar (Marais, 1944). The related species, D. toxicarium, was found to contain  $\omega$ -fluoro-fatty acids (Ward et al., 1964). The toxicity of these plants to livestock (Bell et al., 1955; Peters, 1952) and man (Renner, 1904) led to the discovery of their toxic constituents and to the occurrence of a series of biological transformations that Sir Rudolph Peters has termed "lethal synthesis" (Peters, 1952), and in which monofluoroacetic acid is converted to monofluorocitric acid, a substance of extreme toxicity in the mammalian cell.

Most plant species capable of synthesizing the carbon-fluorine bond are native to Australia and are in the genera Gastrolobium and Oxylobium (FLUORIDES, 1971). Two additional species are known for this property: Palicourea marcgravii in Brazil (de Oliveira, 1963) and Acacia georginae (gidyea), another Australian species (Oelrichs and McEwan, 1961). It may be noteworthy that all of these species are confined to the southern hemisphere.

Because fluorides are emitted into the atmosphere as a result of many industrial processes, including alumina reduction, it was natural to investigate the possibility that synthesis of fluoro-organic compounds is not restricted to a few unique species but that it might be a general, if less prominent, feature



of many species. The answer to this question is of great importance in evaluating the potential hazards associated with environmental contamination by fluoride. Miller and his co-workers (Lovelace et al., 1968; Cheng et al., 1968; Yu and Miller, 1970) reported the presence of large quantities of monofluoroacetic and monofluoro-citric acids in forage, soybean, and crested wheat grass foliage exposed to atmospheric fluoride. But others (Weinstein et al., 1972) were not able to detect the presence of any fluoro-organic compounds in hay, grass, soybean, crested wheat grass, corn, alfalfa, or tomato exposed to atmospheric fluoride or to sodium fluoride solutions. Similar results have been encountered by others but were not published<sup>1</sup>. At present, there has been no published confirmation for the synthesis of fluoro-organic compounds in crops exposed to atmospheric fluoride and one must conclude that the preponderance of available evidence favors the opinion that their synthesis is not a feature common to many other species.

#### The Nature and Distribution of Fluoride Emissions from Alumina Reduction

Alumina reduction results in the emission to the atmosphere of both gaseous and particulate fluorides. Hydrogen fluoride (HF) constitutes the most important gaseous form emitted and its great reactivity and capacity to affect metabolic systems makes it also the most phytotoxic. Cryolite ( $\text{Na}_3\text{AlF}_6$ ) and aluminum fluoride ( $\text{AlF}_3$ ) represent the most important of the particulate emissions. Because phytotoxicity is closely related to solubility, cryolite is much less toxic than  $\text{AlF}_3$ , which is much less toxic than HF. But the less phytotoxic forms of fluoride are of concern when accumulated on or in plants and ingested by domesticated or indigenous herbivores.

The extent of detectable effects of fluoride near alumina reduction smelters will depend upon the effect being measured. If the criterion for an effect is visible foliar injury, the area affected will be much smaller than if the criterion is a

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<sup>1</sup> Personal communications from Dr. Uwe Arndt, Umweltbundesamt, Berlin, West Germany; Drs. John Cooke and Alan Davison, The University, Newcastle upon Tyne, Great Britain; Mr. Ron Hall, Ministry of Agriculture, Fisheries and Food, Newcastle upon Tyne, Great Britain.

measurable increase in the accumulation of fluoride above the background level. Near one alumina reduction smelter in the U.S., it was alleged that an area about 100 square miles had vegetation injury and about 330 square miles contained vegetation that accumulated an amount of fluoride above background. But even in this instance, the area of alleged injury was reduced to about 24 square miles by the next year by improved emission controls and management practices. In most cases, evidence of injury to susceptible vegetation is confined generally to a relatively small area. Because fluoride emissions from a reduction plant usually range from a few hundred to perhaps a few thousand pounds per day, and there are relatively few reduction plants, the contribution of the aluminum industry to global pollution is probably small compared with the enormous amounts of pollutants, including sulfur oxides and fluorides, emitted by combustion of fossil fuels. In fact, many coal-fired power plants emit more atmospheric fluoride than the average reduction plant.

#### Uptake and Accumulation of Fluoride by Plants

One effect that is peculiar to fluoride in plants, and which may not be so well related to air quality as the effects of foliar symptoms, growth, and physiology, is the concentration of fluoride in and by the plant. The important point to be considered with this effect is that damage may result from the production of dental or skeletal fluorosis in livestock that ingest fluoride-containing vegetation, and not necessarily from an effect on the growth and appearance of the plant.

Based on analyses of the plant and studies with the radioactive isotope,  $^{18}\text{F}$  (Ledbetter et al., 1960), it has been shown that the major site of accumulation of fluoride by the plant is the leaf. Once fluoride is accumulated by a leaf, there is little evidence that it is subsequently translocated to other parts of the plant, although Benedict et al. (1965) have reported translocation of fluoride to roots of plants grown at elevated root temperatures.

Once gaseous fluoride has penetrated the leaf, mostly through the stomata, it moves toward the tip and margins of the leaf blade in the transpirational stream (Romell, 1941; Jacobson et al., 1966). It is known that fluoride can be removed from leaves by repeated mild washing procedures, therefore, some transport of fluoride from the interior to the exterior of the leaf must occur. Thus, fluoride is neither uniformly distributed throughout the leaf nor constant in level within the leaf under the influence of normal weathering conditions.

Although the leaf is the major organ of accumulation of fluoride by plants, other parts of the plant usually contain measurable amounts. Some of this may be accumulated from atmospheric exposure, but fluoride in soil or fertilizers may also be a contributing factor, especially to fluoride in roots (Leone et al., 1956).

#### Effects of Fluorides on Plants

##### Symptoms

The most obvious effect of fluoride on plants is the occurrence of foliar lesions. There is considerable variation in the expression of these lesions depending upon the class of plants (narrow-leaved or broad-leaved), their relative susceptibility to fluoride, and the concentration and duration of exposure. Thus, symptoms produced by a high concentration of fluoride for a short duration (acute exposure) may be different from those produced by a low fluoride concentration for a long duration (chronic exposure).

A detailed description of the symptoms produced on plants by acute and chronic exposures is beyond the concern of this discussion; but the symptoms can range from severe necrosis (death) to mild chlorosis (yellowing) of leaves. Occasionally, other organs of the plant can be affected. This type of effect is best exemplified by a condition known as "suture red spot" or "soft suture" of peach fruits which can be induced by a low concentration of fluoride as well as by other agents. The condition is characterized by premature ripening of the flesh

on one or both sides of the suture toward the styler, or blossom, end of the fruit. This localized ripening considerably precedes that of the normal fruit and is often accompanied by splitting of the flesh along the suture. At harvest, the affected areas are soft and often decomposing (Benson, 1959; MacLean et al.<sup>2</sup>).

### Growth, Yield, and Reproduction

As a result of advances in control technology and improved management practices, episodes of acute injury to vegetation near alumina reduction plants in North America have become infrequent. In most cases, a reduction in emissions has resulted in the presence of low ambient concentrations of fluoride. Effects on plant growth and reproductive processes under these conditions are difficult to determine, and even apparently improved growth along transects away from a source are only subjective estimates, since these observed differences may be due to variations in ecologic and edaphic factors. Most of our information on the parameters of exposure that relate fluoride to specific plant responses is derived from experimental fumigations in which plants were exposed to known concentrations of gaseous fluoride, usually as HF, for different periods of time. Unfortunately, much of the information is limited, for technical and other reasons, to: 1) relatively short exposure periods, 2) a limited range of species and varieties of plants tested, 3) an elementary knowledge of the influence of climatic and edaphic factors on plant growth and reproduction, 4) the difficulties inherent in comparing results between laboratories because of differences in equipment, methods of analysis, etc., and 5) only a rudimentary knowledge of the spatial and temporal characteristics of emissions from alumina reduction smelters. Furthermore, the credibility of these experiments in relation to problems of aluminum production is reduced by the experimental difficulties in reproducing the temporal distribution of fluoride and variations in climatic and edaphic conditions. Only recently have new methods been

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<sup>2</sup> MacLean, D. C., L. H. Weinstein, D. C. McCune and R. E. Schneider. Influence of gaseous hydrogen fluoride fumigations on the induction, development, and severity of suture red spot in field grown 'Elberta' peach: A five year summary. In preparation.

devised which enable the study of the effects of long-term, low-level exposures. This means that a significant amount of the published literature has only limited relevance to the field situation.

As is the case with foliar symptoms, the occurrence of effects will depend upon species and varietal differences, the concentration of fluoride, length of exposure, and climatic and edaphic factors. These effects can best be discussed within a botanical framework and their agronomic impact most conveniently described with relation to the intended use of the plant. For example, if a pine tree intended for use as lumber exhibits an amount of needle tip burn insufficient to affect the growth of the tree, there has been no economic loss. The same pine growing as an ornamental specimen in a park or at a private residence would have suffered aesthetically and thereby its worth reduced. Gladioli with fluoride-induced markings on the leaves and flower bracts are unsalable, but if they are being grown for corm production, the foliar effects may have been insufficient to reduce corm yield or quality.

Botanists define growth as an irreversible increase in mass, or as any dimensional change including length, area, or volume. A number of these changes have been associated with atmospheric fluoride including a decrease in radial growth of citrus (Brewer et al., 1960) and Douglas fir (Treshow et al., 1967), dry weights of aboveground portions of roses and citrus (Brewer et al., 1967; Brewer et al., 1960a), weights of sorghum stalks (Hitchcock et al., 1963), leaf size and area (Brewer et al., 1960, 1960a; Leonard and Graves, 1966), weight of alfalfa, orchard grass, and romaine lettuce (Benedict et al., 1964), numbers of flowers or fruits of tomato, citrus, sorghum, or bean (Brewer et al., 1967a; Hitchcock et al., 1963; Leonard and Graves, 1966; Pack, 1966), or weight of roots (Benedict et al., 1964). These published effects represent a broad range of atmospheric fluoride concentrations, durations of exposure, times of exposure in relation to plant

development, and climatic and edaphic factors. Because of the range of conditions covered, it is not surprising to find that there are also many reports where fluoride exposures have not had significant effects on growth and development; e.g., in sorghum (Hitchcock et al., 1963), corn (Hitchcock et al., 1964), gladiolus (Hitchcock et al., 1962), spinach, endive, orchard grass, alfalfa, chard, romaine lettuce (Benedict et al., 1964), tomato (Hill et al., 1958), bean (Pack, 1967, 1969), strawberry (Pack, 1972), or lemon (Thompson et al., 1967). There is also good evidence that exposure to fluoride may stimulate growth as has been reported for Douglas fir needles and shoots (Treshow et al., 1967), total linear growth of citrus and roses (Brewer et al., 1960; Brewer et al., 1960a; Brewer et al., 1967), seed head production in sorghum (Hitchcock et al., 1963), and growth of alfalfa (Treshow and Harner, 1968; Hitchcock et al., 1971) and bean (Treshow and Harner, 1968). It would be naive to accept all the latter information as evidence for the beneficial effects of fluoride to plants since they can be better ascribed to a more twiggy growth in rose and citrus, taller but not necessarily sturdier bean plants, and possibly, under some limited set of conditions, an actual growth enhancement.

#### Physiological Processes

It is obvious that the foliar and fruit symptoms and effects on growth are the result of an alteration in the basic physiologic and metabolic processes involved in plant growth and development. Since a detailed discussion of these effects as the basis for symptom expression is beyond the scope of this paper, we will briefly examine only those physiologic and metabolic processes which have been studied extensively. Thus, photosynthetic carbon dioxide fixation was shown by Thomas (1958) to be reduced by HF. The initial reduction in photosynthesis, however, was greater than the amount of leaf area damaged but after a lag period the reduction in photosynthesis was equivalent to the reduction in leaf area. The extent of the lag period depended upon the concentration of fluoride, duration of

exposure, and species of plant. Foliar respiration (measured as oxygen uptake or carbon dioxide evolution) has been the subject of many investigations, which unfortunately, have resulted in reports of both stimulation (Applegate et al., 1960; Hill et al., 1959; McNulty and Newman, 1957; Weinstein, 1961) and inhibition (Applegate et al., 1960; McNulty and Newman, 1956) of this process. Other reported physiologic and metabolic effects have included increases in enzyme activities, changes in reducing and nonreducing sugars (McCune and Weinstein, 1971; Adams and Emerson, 1961; Weinstein, 1961) and changes in nonvolatile and keto acids (McCune et al., 1964; Weinstein, 1961; Yang and Miller, 1963). The significance of these changes is not known because our knowledge of basic plant processes is incomplete and the experiments are the result of work by many investigators with many plants and under varied conditions.

#### The Biotic Environment

The presence of fluoride in the atmosphere can affect the appearance, growth and development, yield, or form of a plant. But there is also concern that fluoride can alter the plant-disease and plant-insect interaction in the field with respect to environmental transfer of fluoride, ecological imbalance in food chains, decreased yield, or increased cost of production to agriculture or forestry. We are only just beginning to understand these relationships and much work remains to be done. Two types of investigations have been made: (1) those in the field in the vicinity of alumina reduction smelters or other fluoride sources and (2) those carried out in the laboratory under controlled conditions of plant and insect culture and fluoride fumigation.

In laboratory experiments, exposure of beans to HF decreased the incidence and severity of the powdery mildew and bean rust diseases, and increased the incidence of stem collapse from the halo-blight bacterium. The effects of fluoride fumigation on the early and late blight diseases of tomato were not consistent (McCune et al.,

1973). The number of local lesions produced by tobacco mosaic virus in Pinto bean leaves was found to be increased in leaves containing 200-300 ppm fluoride, and decreased in leaves containing more than 500 ppm fluoride, relative to unfumigated control leaves (Dean and Treshow, 1966; Treshow et al., 1967).

Cultures of the Mexican bean beetle on fluoride-fumigated beans resulted in decreased size and mass of the beetles, reduced fecundity with respect to both the number of egg masses produced per female and the number of eggs per mass (Weinstein et al., 1973). If one were to extrapolate these results to the field, one could conclude that exposure to fluoride makes the plant a less suitable habitat for the insect and consequently, less insect injury should occur on crops exposed to fluoride. But this extrapolation has not been supported by field observations. For example, Carlson and Dewey (1971) believed that increased pine needle scale infestation was related to a greater fluoride content of needles, although the results were not statistically significant. No relationship was found between larch case-bearer infestations and distance from an aluminum smelter. Pfeffer (1962-1963) reported that bark beetles and fir leaf roller infestations on fir often appeared before development of fluoride injury symptoms. On the other hand, Compton et al. (1961) and others (Johnson, 1950; Edmunds and Allen, 1956) found no relationship between the fluoride content of ponderosa pine needles and the incidence or severity of pine needle scale or bark beetles.

Increased levels of fluoride have been reported in pollinating, phytophagous, predaceous, and other insects collected near an aluminum smelter (Carlson and Dewey, 1971; Dewey, 1973), but whether the increased levels were caused by ingestion or surface contamination was not determined. An increase in the fluoride burden of bees accompanied by serious effects on the population has been reported many times since 1929 for honey bees near fluoride emitting sources (Kunze, 1929).



Bees do not appear to be susceptible to direct exposure to hydrogen fluoride at concentrations found near aluminum smelters and Weinstein et al.<sup>3</sup> concluded that the reports of fluoride toxicity to bees must be due to ingestion of fluoride in nectar or pollen.

### Is Fluorine Essential for Living Organisms?

The use of fluorine in dentistry and evidence for beneficial effects in bone metabolism have been documented but only recently has evidence been presented that suggests its essentiality for animal growth and development (Messer et al., 1972). A number of studies have been carried out over the last 100 years to determine whether fluorine is essential for plant growth (Thomas and Alther, 1966), but no convincing evidence has been published. One recent report suggested that fluorine is essential for corn growth and development when aluminum is present in the growth medium (Bertrand, 1969). Unequivocal evidence for an essential role of fluorine in plants is still lacking, and until this evidence becomes available, the role of fluorine in plants will be assumed to be nonessential.

### Factors Determining the Effects of Fluoride on Plants

As important as the effects of fluoride, are the conditions that determine the response of plants to this pollutant. One may group these factors as characteristics of the environment, the biologic receptor, and the pollutant itself. Environmental factors may be climatic, such as temperature, humidity, light intensity and quality, photoperiod, and precipitation, and edaphic (soil), such as availability of moisture and essential mineral nutrients. The susceptibility and response of the biologic receptor are also determined by its stage of development and genetic composition. The important features of the pollutant are its physical and chemical

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<sup>3</sup> Weinstein, L. H., D. C. McCune, and A. L. Aluisio. Unpublished.

properties, atmospheric concentration, and duration and recurrency of exposure. Each of these factors can determine the occurrence, type, and degree of effect and can exert its action before, during, or after exposure (with the exception of those factors attributed to the pollutant itself).

#### Stage of Development of the Plant

Stage of development can refer to a period in the life cycle of the plant, such as flowering, or the stages in the life cycle of a single organ, such as a leaf. Perhaps the best information on fluoride effects and stage of development comes from controlled fumigations of sorghum and gladiolus. In the case of sorghum, it was demonstrated that exposure to fluoride during tassel-shooting and anthesis reduced the yield of seeds and aboveground portions of the plant. Exposures before and after this relatively short period in development had no effects on yield (Hitchcock et al., 1963). In part, the observed effect on yield may have been due to an effect of fluoride on stalk elongation or to an effect on leaf mass. Indirect effects on yield by direct effects on leaf mass have been shown for the yield of gladiolus corms (Hitchcock et al., 1962).

For the most part, effects on susceptibility refer to the presence or degree of leaf injury rather than to yield. In this case, it is generally assumed that immature leaf tissues are most susceptible to fluoride, as in the case of ponderosa pine where elongating needles are highly susceptible and mature needles are quite resistant (Adams et al., 1956). This clear distinction, unfortunately, is blurred by the latency of some fluoride effects and their expression, and it is not unusual to observe necrosis on fully elongated pine needles where they have accumulated enough fluoride to be injured when environmental stresses occur later in the season. The susceptibility of immature foliage holds not only for the conifers but also for the narrow- and broad-leaved species.

### Species and Variety

For reasons not yet understood, plants exhibit an extremely broad range of tolerances to fluoride, as well as to other air pollutants. Great differences in susceptibility are found not only between different species but also between varieties of the same species. The resistance of species such as camellia, cotton, and celery to fluoride may be contrasted to the extreme susceptibility of gladiolus, Chinese apricot, Italian prune, and developing needles of ponderosa pine. This differential response may also be found among varieties of, for example, gladiolus (Hendrix and Hall, 1958; Hitchcock et al., 1962), sweet corn (Hitchcock et al., 1964) and sorghum (Hitchcock et al., 1963), although the degree of difference is not as great. The white-flowered gladiolus variety 'Snow Princess', for example, has been reported to be five times more sensitive to fluoride than the lavender-flowered variety 'Elizabeth the Queen' (Hitchcock et al., 1962). A similar situation has also been observed among certain conifers, such as ponderosa pine, which is made up of phenotypic variants among the natural population, each tree having a somewhat different genetic complement, and showing great differences in their response to fluoride.

### Environment

Although the atmospheric concentration of fluoride, the duration and frequency of exposure, age or stage of development of the plant, and species and variety are the major factors associated with plant susceptibility, most climatic and edaphic factors also exert important effects on plant response.

Plants exhibiting a water deficit have been shown to be more resistant to fluoride than those receiving adequate water (Daines et al., 1952; Zimmerman and Hitchcock, 1956). It is clear also that light plays a role in modifying the response of plants to fluoride. With sensitive species, injury was shown to occur in both light and darkness at about the same foliar fluoride-contents,

while with resistant species, injury was observed in the dark when the foliar fluoride accumulation was only about one-half of that in the light (Adams et al., 1957). Other investigators have reported that fluoride accumulation in the tissues of plants was greater in the light than in darkness and concluded that uptake of fluoride into foliar tissues was lower in the dark because stomata were closed. Suboptimal nutrient supplies of calcium, magnesium, potassium, phosphorus, and nitrogen have been associated with increased severity of fluoride-induced markings (Weinstein and McCune, 1970).

Pollutants themselves must also be regarded as environmental factors since under ambient conditions they occur in various combinations. Little is known of the modifying influence of other pollutants in the presence of fluoride, but evidence was recently presented that the presence of  $SO_2$  increased the production of foliar lesions, decreased yield, and reduced fluoride accumulation in sweet corn (Mandl et al., 1975).

#### Dose-Response Relationships

The relation between dose and response depends upon many factors, such as species or variety, stage of development, environmental conditions, recurrency or frequency of exposures and the particular response that is being measured. Thus, one could describe the relationship between concentration of pollutant and length of exposure to produce a single effect, such as foliar injury to a particular species. But the shape of this curve would vary according to the parameter that is being measured, so that the curves describing effects on growth and yield, visible injury, or metabolism would be different (Figure 2).

McCune (1969) summarized the known published literature with respect to the pollutant concentration and duration of exposure (dose) that have produced a threshold effect in a number of types of plants (Figure 3), and the wide range of plant tolerance to fluoride can be seen. Although most published experimentation

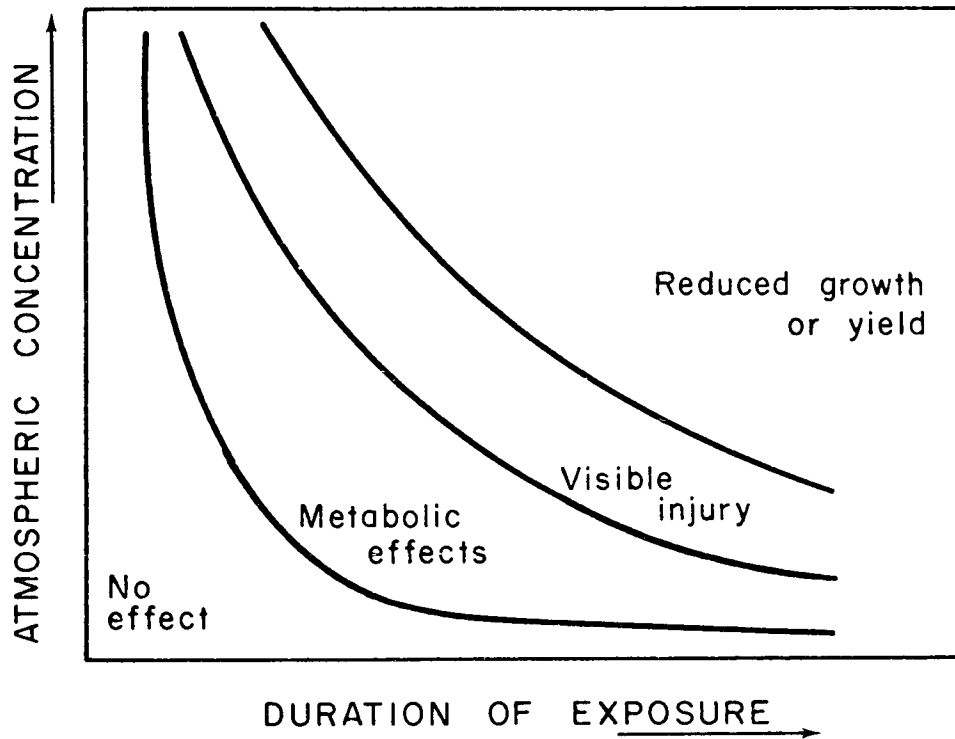


Figure 2. Dose-response of atmospheric fluoride and effects produced.

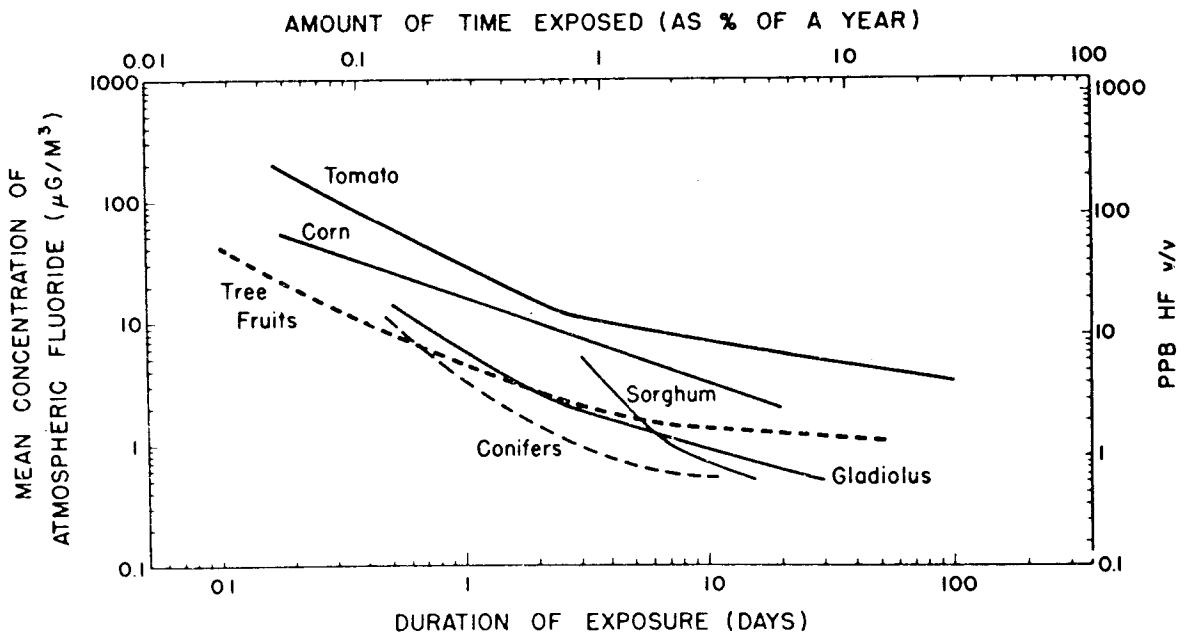


Figure 3. Possible air quality criteria for atmospheric fluoride effects on different plant species (McCune, 1969).

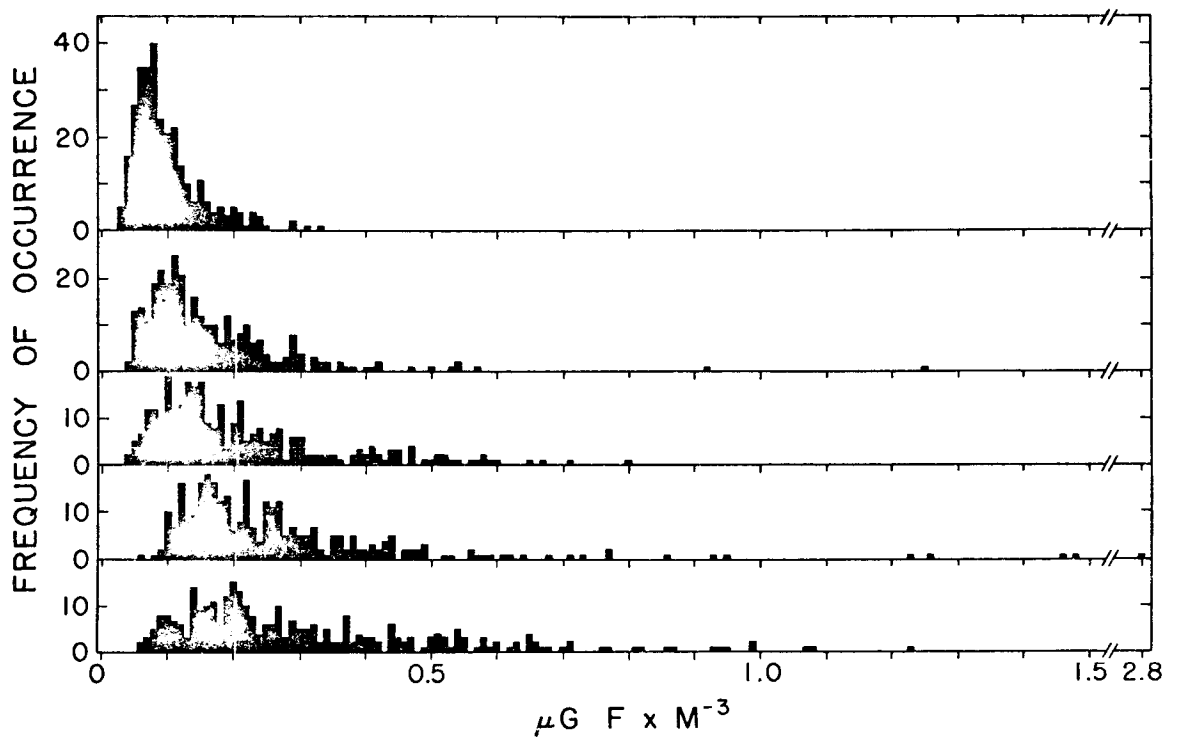


Figure 4. Frequency distribution histograms for gaseous fluoride concentrations at five different sites around a source (after McCune et al., 1975).

was designed as a simple dose-response relationship, less emphasis has been placed on another characteristic of the field exposure, recurrency. The effect of a continuous exposure to HF for seven days may be very different from the effects of exposures at the same concentration for seven days spaced over a month, a growing season, or a year. This led Adams and Emerson (1961) to conclude that the sequence of exposures may outweigh in importance the actual level of fluoride used within a range of concentrations. This is an important point and one that has not been addressed extensively; but MacLean and Schneider (1973) found that accumulation of fluoride by forage was greater after continuous exposure than when the same dose was provided in alternate 48-hour exposures.

That constant concentrations over relatively long periods do not appear to be encountered in the field is readily seen in the data compiled by McCune et al. (1975) who prepared frequency histograms to describe ambient fluoride concentrations at five sites around an alumina reduction smelter (Figure 4). These histograms represent 12-hour mean values for a 5-month period during the growing season. Several facts become immediately apparent. First, ambient fluoride concentrations are not distributed uniformly, but there are infrequent peaks superimposed upon a preponderant distribution of much lower concentrations, and zero values occur frequently. Second, these distributions reflect not only emissions from the smelter but local meteorological and topographical conditions as well as sampling and analytical error. Only recently have attempts been made to simulate realistic exposures of fluoride to plants by the utilization of the type of data shown in Figure 4 to identify the significant characteristics of the field exposures.

#### Alumina Reduction and Fluoride Pollution: The Future

Improved air cleaning methods, the promulgation of emission standards, and more appropriate plant site selection in the U. S. will result in increasingly



lower ambient concentrations of fluoride. No longer will our major concern be that of serious vegetation damage because of poorly controlled emissions; rather, localized episodes will be emphasized. But several questions with respect to fluorides and plant life will remain to be solved, among which are the following: (1) effects of long duration, low level exposures on plant growth, yield, quality and fluoride accumulation; (2) possible latency of effects, e.g., on evergreens over several years; (3) effects of field exposures on plant populations and community structure; (4) effects of particulate fluorides derived from alumina reduction, alone and in combination with gaseous forms; (5) interactions of fluoride with other gaseous pollutants, such as  $SO_2$ , also emitted in alumina reduction; (6) effects of fluoride on the susceptibility or suitability of plants as habitats or hosts for insects and diseases.

Where will the funds come from to support this research? In the past, the most important continuous source of support for fluoride research on plants in North America has been the aluminum industry, which has contributed to a program of research at the Boyce Thompson Institute for 25 years. Another major source of support for fluoride research has been the U. S. Environmental Protection Agency and its predecessor organizations. One would hope these sources will continue to recognize the need for research on the effects of fluorides on plants and plant systems.

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**UNITED NATIONS  
ENVIRONMENT PROGRAMME**



Fluoride Effects on Animals and the Aluminium Industry

J. W. Suttie

Department of Biochemistry  
College of Agricultural and Life Sciences  
University of Wisconsin-Madison  
Madison, Wisconsin 53706

Animals normally ingest small amounts of various fluorides in their rations with no harmful effects, but excessive ingestion can be damaging. Excessive intake of fluoride by domestic animals has resulted from the consumption of high fluoride waters or mineral supplements, but has most often been associated with the ingestion of forage which has been contaminated with fluorides contained in industrial emissions. Large amounts of fluorides are released from various industrial processes such as; aluminum reduction, phosphate processing, steel manufacturing, brick and tile production, and combustion of coal for various purposes. Animal health problems associated with excessive fluoride intake have been observed around most of these industries, and a number of such exposures have been reported (1-8) near primary aluminum smelters. It has been estimated that only about 15% of the total fluoride emissions from these industrial sources in the United States in 1968 were from the manufacture of aluminum. Although its contribution toward total worldwide fluoride emissions has therefore been relatively small, the aluminum industry has been responsible for a significant percentage of the known incidence of damage to livestock by industrial emissions, and it is a problem that must be dealt with in any consideration of the relationship between the aluminum industry and the total environment.

#### ROUTE AND TYPE OF FLUORIDE EXPOSURE

In the field, livestock are exposed to fluorides from the ambient air, from ingested fresh forage or hay, from feed supplements, and from the water supply. There is also the possibility that a significant amount of



high-fluoride soil, through rain splash or windblown dust, may contaminate forage. Of these possible sources of fluoride in the ration, only that in the atmosphere and a portion of that in fresh or cured forage is contributed by industrial emissions.

Aluminum is produced by the direct electrolytic reduction of Alumina ( $Al_2O_3$ ) in large reduction cells or "pots". The electrolyte in the cells consists of alumina dissolved in a mixture of cryolite ( $Na_3AlF_6$ ) and other fluoride salts. In this mixture, it is possible to carry out the reduction at a temperature of about  $1000^{\circ}C$ . During the reduction process, fluoride containing gases, mainly HF, are emitted from the cell, as well as fluoride containing particulate matter such as cryolite, aluminum fluoride and calcium fluoride. To the extent that these fluoride containing materials in the effluent gases are not collected and scrubbed, they pose a potential hazard to livestock in the area. In addition to direct fluoride emissions from the pots there is a possibility that fluoride coated alumina particles from a dry scrubbing system may become dispersed to the atmosphere and contribute to fluoride emissions from the plant.

It is usually assumed that the direct inhalation of fluoride from the atmosphere contributes a negligible amount to the total fluoride intake of animals in an area of industrial pollution. However, there is little data in the available literature which directly deals with the question of the hazard to livestock due to inhalation of fluoride from the ambient air. Rough calculations of the amount of air inhaled per day by a cow of average size indicate that the amount of fluoride that can be absorbed by this route is very small. The major source of fluoride in the ration of livestock in areas with a fluoride pollution problem is therefore the ingestion of

fluoride contaminated vegetation. The factors that affect the accumulation of fluoride in vegetation and the attempts to correlate ambient fluoride concentrations with accumulation in vegetation have been discussed in this seminar by Dr. Weinstein. Gaseous forms of fluoride are absorbed by the foliar tissues and move to the marginal or apical portion of the leaves. Much of the fluoride containing particulate matter emitted from a reduction plant is submicron in size and to some extent these small particles are dissolved in moisture which is bound to the foliar surface and the soluble fluoride absorbed. Some fluoride containing particulate matter is however simply deposited on the surface of the vegetation where it also contributes to the fluoride intake of animals consuming the vegetation.

The fluoride content of forage crops in areas subject to atmospheric fluoride pollution has been found by most investigators to be extremely variable, and this factor must be considered in assessing the potential for damage. In general, the fluoride content is less during the early part of the summer, when the forage is growing rapidly, and rises during the fall. During periods of rapid growth, the accumulation of dry matter causes a continual dilution of fluoride. During the late fall or during a drought, dry-matter accumulation slows down and may even decrease, with a corresponding increase in forage fluoride concentration. The reluctance of cattle to graze dry unpalatable forage also influences the extent to which this source contributes to the fluoride content of their ration. Because forage that is cut and dried for hay often represents the rapid vegetative growth of the early part of the summer, its fluoride content is more like that of the low-fluoride spring pasture than that of the fall and winter pasture.

Natural vegetation, even in areas far removed from any industrial sources of fluoride contains some fluoride (9), and although this varies considerably it is often found to be between 2.0 and 4.0 ppm.

#### SYMPTOMS OF THE TOXICITY

The ingestion of excessive amounts of fluoride by animals leads to the development of a number of characteristic symptoms. A number of reviews of these general effects are available (10-13) and there are two recent National Research Council publications<sup>(14,15)</sup> dealing with this problem. Our present knowledge of the effects of fluorides on domestic animals has been gained from observations of field cases of the toxicity, and from controlled experimental studies. The general effects of the toxicity are similar in most species and can be briefly reviewed as follows.

#### Dental Lesions

The most obvious signs of the toxicity are the abnormalities in the permanent incisor teeth caused by the ingestion of fluoride during the developmental period (roughly 6-30 months of age in cattle). The ameloblasts, which produce the organic matrix of the dental enamel are reduced in size and an abnormal matrix, which fails to achieve normal calcification is formed. The effects of these histological changes in the incisor enamel are generally described as chalkiness (a dull chalk-like appearance), mottling (a pattern of chalk-like patches in the teeth), and hypoplasia (a thin enamel). In addition to these visible alterations, an affected tooth is subject to more rapid wear and in some cases to an erosion of the enamel away from the dentin. These changes in the teeth can be given a numeric score based on severity of the lesion, and a

standardized system has been developed (15) which can be used to objectively score the fluoride induced effects. This scoring system is shown in Table 1, and some examples of the types of incisor lesions which are seen are shown in Fig. 1.

The molar teeth of an animal are being formed during the same general period as the incisors and, if subjected to increased exposure to fluoride, will also develop a defect. This lesion is evident mainly as an increased rate of molar attrition and the development of an uneven molar attrition line which results because of the more severe effects on one molar than on another. This effect, which is perhaps of more importance to the health of the animal than the accelerated wear of the incisors is illustrated in Fig. 2.

#### Osseous Lesions

The extended ingestion of toxic amounts of fluoride can result in a number of lesions of the skeleton. The affected bones lose their normal, hard, smooth luster, and when cleaned appear rough, porous and chalky white. In severe cases it is possible to observe an exostoses of the long bones caused by a severe periosteal hyperostosis. A second skeletal lesion which has frequently been observed is a calcification of the joint tendons at the point where they attach to the leg bones which can eventually cause an ankylosis of the joint. Examples of these lesions are shown in Fig. 3. Accompanying the gross changes observable on the surface of the bones and joints there are extensive fluoride induced histologic changes. These alterations appear to be very similar to those responsible for the production of abnormal enamel in developing incisors.

### Lameness

A lameness or generalized stiffness is an intermittent sign of fluoride toxicity and is often difficult to distinguish from lameness caused by a multitude of other agents or injuries. The clinical basis for this lameness is not clear, it is probably multicausal but does not appear to be associated with the general exostotic type of periostial hyperostosis. A specific lameness which has been observed in cattle in some geographic regions appears to be associated with a fracture of the third phalanx or pedal bone, which is the last bone in the foot. This lesion has not commonly been observed in experimental studies and the reason for its increased incidence in some areas is not clear.

### Systemic Effects

Appetite impairment, eventually resulting in decreased weight gain, cachexia, and diminished milk yield is an important factor in the development of the advanced stages of fluoride toxicity. Because an effect on appetite is common to so many deficiency and toxic states, it is not in itself a good diagnostic criterion. There is no evidence to indicate that fluoride ingestion can directly influence the physiologic process of milk secretion, and any effect noted on productive ability in any species has been found to be secondary to other responses.

### Chemical Evidence

The fluoride content of skeletal tissues gradually increases with age as bones accumulate fluoride at a rate which is to a large extent dependent on the fluoride concentration of the ration. Analyses of skeletal tissues,

which can best be obtained at autopsy, or in live animals by rib or vertebral biopsy, are, thus, one of the most definitive criteria of the toxicity, and the magnitude of such increases are shown in Table 2. Sufficient experimental evidence is available for most species so that it is possible to correlate the various clinical signs of the toxicity, the fluoride intake, and the skeletal retention of fluoride. Much of the ingested fluoride is excreted in the urine, and analysis of urinary fluoride may, therefore, be used to obtain a rough indication of dietary intake. The fluoride content of blood and soft tissues is very low, and increases only slightly with increased intake. The small magnitude of this increase and the low concentrations present make these analyses difficult, and decreases their value as diagnostic tools.

Most of the available data which can be used to relate various fluoride-caused lesions to concentrations of fluoride in the diet have been obtained from experiments where animals were fed a constant amount of fluoride for an extended period. This consistency of intake is not always present in field cases, and recent studies (16, 17) have suggested that the alternate high and low intakes that might occur in the field are somewhat more damaging to animals than if the same yearly amount of fluoride was fed at a constant intake level over the year. This study indicated that the skeletal retention of fluoride is a good measure of the total exposure to fluoride (Table 3) but that the effects on the developing dentition are largely a reflection of the fluoride exposure at the relatively short time that each pair of incisors is being formed. It is therefore possible that an animal may have a skeletal fluoride level

which would normally be considered safe, but which would have to be considered adversely affected because it had been exposed to a sufficiently high level of fluoride for a short time to damage one or more pair of incisor teeth.

#### SPECIES TOLERANCE

Sufficient data are now available to set tolerance levels for fluoride ingestion by most domestic species (Table 4). The data used to determine these tolerances have been obtained over a number of years by various investigators, and they have been critically discussed (15) in a recent publication of the U. S. National Research Council. The tolerances have been set by considering the economic usefulness of various species and by determining what effect various types of lesions might have on this usefulness. In this sense, a stated tolerance level would indicate a level of fluoride ingestion that, on the basis of published data for that species, could be fed without clinical interference with its normal performances. Such a tolerance level would not insure that animals might not show some signs of elevated fluoride ingestion as long as these did not affect the performance of the animals. It should also be remembered that in considering the effects of fluorides as industrial pollutants, only those species which graze on contaminated forage will be affected. Finishing beef cattle and lambs, swine, and poultry are fed rations containing largely the seed portion of cereal grains. This portion of the plant remains relatively low in fluoride content even in areas of high exposure to atmospheric fluorides.

## Cattle

Much of the available experimental work on the influence of fluorides on livestock has dealt with the effect of excessive fluoride ingestion by dairy or beef cattle, and most of the problems which have developed around aluminum smelters have also involved cattle. The data summarized in Table 5 indicate that young heifers fed in excess of 50 ppm fluoride through maturity and production will show all of the general signs of fluoride toxicity. The table also indicates that if the fluoride level is maintained under 40 ppm, the only definite signs of the ingestion will be a slight periosteal hyperostosis and some incisor mottling. This mottling should not be associated with enamel hypoplasia or an increased rate of wear of the incisors. These animals will show an increased urine and skeletal tissue fluoride concentration, and a slight but insignificant increase in soft tissue fluoride. Histologic changes in bone and tooth structure which have no known effect on the well-being of the animal may also be seen at ingestion levels below 40 ppm. When these considerations are taken into account, it appears that the fluoride concentration in the diet of young cattle being raised for milk production or as replacements for beef herds should not exceed 40 ppm F. The available data would also indicate that beef or dairy cattle first exposed to elevated fluoride intakes after the permanent dentition is formed can be fed as much as 50 ppm F in their diet without influencing performance. Finishing cattle will not be held for a sufficient time for dental lesions to become serious, and the available data would indicate that as much as 100 ppm F can be tolerated in the diet of beef heifers or steers being finished for slaughter.



### Sheep, Horses, and Swine

Most of the extensive experimental work on fluoride effects has involved cattle but there have been a number of studies utilizing sheep. These studies indicate the sheep being raised for lamb or wool production can tolerate 60 ppm F as a soluble fluoride in their diet. No carefully controlled studies have been conducted to determine the effects of excessive fluoride ingestion on horses. Several workers have noted that affected horses are found in the same geographic areas in which cattle have been injured by fluorides from industrial effluents. Analysis of pastures in these areas would suggest that 60 ppm F is the tolerance level for this species. Only limited studies of the effects of fluorides on swine have been conducted, but the available data would indicate that both finishing pigs and breeding sows can tolerate at least 150 ppm F in their diet.

### Poultry

The available data indicate that poultry are relatively resistant to fluoride effects, and suggest that growing chicks can tolerate 300 ppm F in the diet, and that laying hens can tolerate 400 ppm F. The data on tolerance of turkeys is even more limited, but what information is available would suggest that growing turkey poults can tolerate about 400 ppm F.

### Wildlife

Concern has been expressed for the safety of wildlife in areas surrounding aluminum reduction plants. A limited amount of analytical data indicates that, as might be expected, skeletal fluoride concentrations

of deer and elk in such areas have been increased. There seems no real basis for assuming that these animals are any more susceptible to the adverse effects of fluoride ingestion than other herbivores, and it is generally felt that if the most sensitive domestic species, cattle, are protected, then the area will be safe for wildlife.

#### LIVESTOCK DAMAGE AND THE ALUMINUM INDUSTRY

The aluminum industry is therefore responsible for the emission of significant amounts of fluoride to the atmosphere, and fluorides have been shown to be toxic to a number of animal species. As might be expected, problems have developed.

#### Past Performance of the Industry

The past history of the industry relative to livestock production in the areas where aluminum reduction facilities have been built is a story of increasing awareness of the environmental problems involved. Aluminum production was a relatively insignificant industrial process before World War II, and a large increase in reduction capacity was achieved during the early 1940's. During this period the potential seriousness of the problem was not realized, and little attention was paid to pollution abatement. Consequently, large quantities of fluorides were released to the atmosphere. As might be expected, the environmental impact of the emissions in some areas was disastrous and local farmers and ranchers suffered severe losses to their dairy, beef cattle, and sheep herds. In some cases the individual companies involved were able to reach amicable agreements with the farmers and ranchers regarding terms of financial settlements for past damages, and in other cases, lengthy bitter lawsuits which had a

lasting effect on relationships within the community ensued. Although factual information is not generally available, it is doubtful that, during the 1940's to 1950's, there were any aluminum reduction facilities located in regions where there were significant livestock populations within a few miles of the plant that did not cause some degree of damage to this population because of their fluoride emissions.

#### The Industry in Recent Years

Although the aluminum industry did profit somewhat from its past problems, a number of aluminum reduction facilities built in the late 1950's and early 1960's have subsequently been involved in the historical problems of livestock damage, compensation for damage, and lawsuits. The reasons for this are numerous. Although increased attention was given to pollution control equipment, the efficiency of both fume gas collection and the removal of fluorides from this gas was less than is possible with current technology. A large number of factors go into the selection of a new plant site, and locating a reduction facility in an area where there would be a decreased potential for livestock damage was almost always a minor consideration. A third problem has been the lack of a sufficient amount of land around the actual plant site to create a buffer zone on company owned property. The production of a pot line can be increased by altering the conditions of operation and increases in production have usually resulted in an increase in the total emissions of fluoride which has further contributed to the problem.

#### Imposition of Standards

With the potential for damage present, and the past record of verified damage to livestock, it is understandable that governmental agencies have

moved toward the imposition of air pollution standards which would protect livestock in the area around primary aluminum smelters. Standards designed to protect animals from the effects of fluorides in the atmosphere could presumably be set at any one of three levels; atmospheric fluoride concentration, forage fluoride levels, or the effects on the animals exposed. The atmospheric fluoride concentration can be determined with equipment and methods available, however, continual monitoring of large areas over an extended period would be required. Even if ambient fluoride concentrations were known, the effect of variations in the chemical form of the fluoride emission, growth rate of the plants, rainfall, etc. on the rate of fluoride uptake by vegetation make it difficult to relate these values to forage concentrations. What information is currently available to predict forage fluoride concentrations from ambient concentrations seems inadequate to use these values for standards.

The effects of fluoride on cattle and other livestock can be assessed and evaluated, and could presumably be used as a basis for standards. However, because of the long latent period before many of the symptoms develop, the damage might be done before the problem is recognized. The increases in fluoride content of the urine or plasma are an indication of exposure but are too subject to short term variation to be useful as a standard. Fluoride analysis of a vertebral biopsy would stress the accumulative nature of the toxicity but do not seem feasible as a routine survey method.

Forage fluoride levels can be determined, and although there are problems of collection and analysis, levels of forage fluoride appear to be the only

feasible standard (18) and limits on forage fluoride levels have been established by a number of governmental regulatory agencies. An alternate approach is to limit the emissions in terms of pounds of fluoride per ton of aluminum produced. It is very difficult to relate this to possible effects on animals because of the large number of variables involved in the different meteorological and climactic conditions present at various sites.

When standards are established some consideration must be given to a definition of what physiological responses in the receptor being considered, in this case livestock, the standard is designed to protect. In the case of fluoride ingestion, the effects on livestock can be conveniently placed in three categories: economic effects, severe dental fluorosis, and nondamaging evidence of fluoride ingestion. At sufficiently high levels of intake animals have been observed to become lame, exhibit severe exostotic lesions, develop severely worn incisor and molar teeth, and to have their productive ability in terms of milk or calf production decreased. Obviously, such economic effects can not be tolerated. At somewhat lower levels of intake investigators have not been able to demonstrate any loss of productive ability of animals but have found that severe dental fluorosis is present. These animals will possess one or more pair of incisors which demonstrate enamel hypoplasia (score of 4 or 5, Table 1) and which will show an increased rate of attrition. Even though it may not be possible to prove that an animal in this condition has in any way had its productive ability impaired, it is obviously of less value to the farmer or rancher if he tries to sell it, and he should be protected from the possibility that such damage may occur. At ingestion levels much below those required

to produce enamel hypoplasia, a trained observer can detect alterations in enamel structure, and there will be chemical evidence of an increase in skeleton, urine, and soft tissue fluoride. There seems to be no justification for setting a standard which will prevent these discernible deviations from normal in animals which do not influence their general health, productive ability, or the soundness of their dentition. It has also become increasingly apparent that animals must be protected against short periods of high level exposure that might damage the dentition even though the long term ingestion level is in a safe region.

Based on a consideration of these factors, a standard of the following type has been adopted by a number of regulatory agencies. Fluoride emissions should be regulated so that:

- A. The yearly average (monthly samples) fluoride content of the forage does not exceed 40 ppm (dry wt.) and
- B. The fluoride content of the forage does not exceed 60 ppm F for more than two consecutive months, or does not exceed 80 ppm F for more than one month.

In areas where cattle are not grazed continually, but are fed cured forage, as hay, during the winter, the forage fluoride content of the hay is taken to represent the forage fluoride content for as many months as it is fed in establishing the yearly average.

#### Present and Future Performance of the Industry

Present technology is such that new aluminum reduction plants can be built with design specifications such that less than two pounds of fluoride may require a secondary roof scrubbing system, but it would appear that a level of three pounds per ton can be achieved with a primary scrubbing system.

Assuming some type of reasonably favorable climatic and meteorological conditions, and smelters in the 150-200,000 ton per year capacity range, this level of emission will restrict forage levels which are in excess of the types of standards which have been proposed for relatively short distances from the plant. They should in fact be limited to an area that could reasonably be expected to be encompassed by the plant site. Even assuming the present design technology, the compatibility of an aluminum reduction facility and livestock production in the immediate area will depend on a number of factors. Foremost is perhaps continued maintenance of the entire fume control system, and supervision of labor in the pot rooms. A well designed and engineered scrubbing system is of no value unless it is properly maintained, and fume collection is as efficient as calculated. If workers are careless about closing doors in the hooding system which must be opened to work the pots, fluorides will escape the scrubbing system and be emitted to the atmosphere. The same situation will occur if the hood and duct work systems are not repaired as they develop leaks. An additional problem in modern dry scrubbing systems is the large mass of high fluoride alumina which is moved throughout the plant. To the extent that this dusty material is allowed to accumulate on the premises, some of it will be blown from the building and contribute fluorides to the atmosphere. Although this rather large particulate matter is not dispersed very far, it can be a significant factor in increasing forage fluoride concentrations close to the plant.

In the future, additional consideration must be placed on site location, and on placement of the actual plant facilities on the site. An area where there is a relatively high concentration of cattle should not be

considered as a site for an aluminum reduction plant unless it is clear that sufficient land, particularly in the direction of the prevailing winds, can either be purchased by the company or if some type of an easement limiting liability can be obtained from the farmer. It should also be recognized that designing a plant to limit the amount of fluoride emitted as a function of aluminum production is of little value as a protection against pollution if the size of the plant is sufficiently increased. That is, two pounds of fluoride per ton of aluminum from a 200,000 ton capacity plant will have the same environmental impact as the release of four pounds of fluoride per ton of aluminum from a 100,000 ton capacity smelter. This raises a legitimate question of whether or not, in an attempt to minimize the environmental hazard, there should be some limit to the size of an aluminum plant that might be constructed.

#### PRACTICAL SIGNIFICANCE OF FLUORIDE EMISSIONS

The impact of a given emission of fluorides from a plant upon animals in the area, is of course dependent on a large number of factors. There are a number of rather large reduction facilities in operation which do not have the most modern control technology but which have never had any ~~problem~~ with livestock damage because of the lack of a significant number of animals in the area. On the other hand, some relatively new plants with efficient fume collection and scrubbing systems have had to be very concerned with possible damage because they were placed in areas where there were large numbers of animals adjacent to the plant site. Because of the large number of variables involved, it is difficult to make real firm estimates of the area around an aluminum reduction plant in which



there might be a problem. However, based upon a very limited amount of information in the literature, and upon situations I have observed at a number of plants, it is possible to get a general idea of the magnitude of the problem. Figure 4 gives an indication of the area that might be adversely influenced in the vicinity of a rather large (150-200,000 ton) reduction plant assuming three different degrees of technology. The figure indicates both the area where animals might suffer either some economic damage, or at least have a sufficient degree of dental fluorosis to be considered damaged, and also a considerably larger area where it would be possible to observe some dental effects in the animals, but where this degree of dental fluorosis should have no effect on the health of the animals. The size of the areas involved can not really be determined from any type of data which is publicly available, but merely represents what seems to me to be a reasonable figure based upon my personal knowledge of the situation that is known to exist around a number of aluminum reduction plants in the United States and Europe. It should therefore be considered only a rough approximation and can in no way be applied to a specific facility.

How many animals might be influenced under these conditions would depend of course on the animal population density in these areas. The state of Wisconsin, which has no aluminum industry, has about twice as many milk cows as any other state in the United States. Within those counties of Wisconsin which lead in milk production, there are about 60 cows per square mile. Assuming this figure, Figure 4 also indicates the number of cows that might potentially be influenced if an aluminum

reduction plant were built in the dairy areas of Wisconsin. Whether or not these numbers seem large depends upon your viewpoint. There are almost two million dairy cows in Wisconsin, so that even a thousand cows is an insignificant portion of that number. On the other hand, a thousand cows would represent a few percent of the animals in many counties in Wisconsin, and the adverse effects of fluorides on even a few hundred cattle would have a significant influence on a given local community and would of course include the entire herds of those few farmers\*close to the source. These numbers do, I think, serve to point out that the potential harmful effects to livestock from the aluminum industry are very local. Although they can be serious, and may in fact make it impossible for some farmers to continue in their desired type of agricultural endeavor, the total impact on the livestock industry is negligible.

This again suggests that if the total economy is considered, we would be better served if it were possible to more effectively separate by wise zoning laws certain industrial processes and types of agricultural operations. A considerable percentage of the approximately 1500 dollars per annual ton of capacity needed to construct a new aluminum reduction plant is spent for air pollution equipment. Many types of agricultural endeavors are not adversely influenced by the level of fluoride pollution which has existed in the vicinity of most of the aluminum reduction plants which have operated world wide during the last 20-30 years. If some mechanism were available to separate a specific incompatible agricultural practice, such as dairying, from an industrial operation such as an aluminum reduction plant, the cost of pollution control could be

significantly decreased, and considerable savings to the total economy could result. This could be done without compromising any concern about the effects of fluorides on human health. Such planning would however necessitate a degree of governmental control over both private industry and agriculture that is perhaps not possible, or desirable, in most societies. Even without a definite plan of this type, it seems that the potential for avoiding adverse effects arising from fluoride emissions might become more of a factor in the location of aluminum reduction plants than has been the case in the past.

SUMMARY

The emissions of fluoride from aluminum reduction plants has resulted in the accumulation of fluorides in the vegetation surrounding the facilities to the extent that there is a hazard to livestock production. The effects of fluorides on animals, which chiefly involve defects in the developing dentition, and skeletal lesions have been extensively studied and well documented. It is possible therefore to determine the level of fluoride that can be tolerated in the area surrounding a plant site and to get an approximation of the area which might potentially be adversely influenced by a particular plant. By a combination of improved emission control systems, and a consideration of the existing livestock population when choosing a site, it should be possible to build new aluminum reduction plants that have little if any adverse effect on livestock in the area.

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Figure Legends

Fig. 1. Typical examples of types of lesions produced in permanent bovine incisors by fluoride ingestion. Animals were first exposed to fluoride at 2-5 months of age. Fluorosis scores, reading from the first incisor to the canine tooth, are as follows: animal A, 1-1-1-1; animal B, 3-4-4-4; animal C, 2-4-2-5; animal D, 5-5-5-5.

Fig. 2. Effect of fluoride ingestion on wear of permanent bovine molars. Animals were fed <sup>the</sup> indicated amount of fluoride from age of a few months to 6 years. Note even attrition line in control animal and uneven wear seen when fluoride was ingested during formative period.

Fig. 3. Examples of fluoride-induced lesions on long bones. Examples shown are bovine metatarsal bones from cattle that were fed the indicated amounts of fluoride from age of a few months to 6 years. Note generalized periosteal hyperostosis and prevalence of sharp exostotic lesions on some bones. Effects of fluoride ingestion on bones can be extremely variable and a given level of intake does not necessarily have a reproducible effect on bone.

Fig. 4. Approximate areas surrounding an aluminum reduction plant where effects on livestock might be seen. In each case the darker area represents the region where cattle might suffer economic damage or at least severe dental fluorosis (score 4 - 5). The lighter area represents that region

Figure Legends, continued

(Fig. 4, cont.)

where it might be possible to detect alterations in the dentition (score 2 and 3) which differ from normal but do not adversely influence the performance of the animal. The numbers indicate the cattle population that might be in an area of this size if a plant was located in a typical Wisconsin dairying region. The number of animals indicated below the lighter cow head represents the number in both the dark and light area around each plant.



Table 1

## Bovine Dental Fluorosis

<u>Score</u>	<u>Appearance of Incisor</u>
0	<u>Normal</u> smooth, translucent, glossy white appearance of enamel; tooth having normal shape
1	<u>Questionable Effect</u> slight deviation from normal, exact cause not determinable; may have enamel flecks but is not mottled.
2	<u>Slight Effect</u> slight mottling of enamel, best observed as horizontal striations with transmitted light; may have slight staining, but no increase in normal rate of wear
3	<u>Moderate Effect</u> definite mottling; large areas of chalky enamel or generalized mottling of entire tooth; tooth may have a slightly increased rate of wear and may be stained
4	<u>Marked Effect</u> definite mottling, hypoplasia, and hypocalcification; may have pitting of enamel; with use, tooth will have increased rate of wear and may be stained
5	<u>Severe Effect</u> definite mottling, hypoplasia, and hypocalcification; with use tooth will have excessive increase in rate of wear and may have erosion or pitting of enamel. Tooth may be stained or discolored.

Table 2

Effect of Fluoride Concentration in the Ration  
and Period of Exposure on Skeletal Fluoride

Fluoride in Ration	Rib F Conc. (ppm dry fat-free wt.)			
	1 yr	2 yr	3 yr	4 yr
12 ppm	300	400	600	800
27 ppm	800	1300	1500	2100
49 ppm	1700	2100	3000	4100
93 ppm	3100	3700	5300	6800

Holstein heifers were started on experiment at 3-4 months of age and rib biopsies taken at the times indicated. The values are means of 5 animals in each group and have been recalculated from data in Shupe, J. L., et al., Am. J. Vet. Res. 24, 964 (1963).

Table 3

Effect of Variations in Pattern of Fluoride Intake  
on Skeletal Fluoride Retention

<u>Fluoride Intake, mg/kg of Body Wt.</u>		<u>Vertebral Fluoride Content (ppm ash wt.)</u>	
<u>Actual</u>	<u>Yearly Average</u>	<u>1 Year</u>	<u>2 Years</u>
1.5 for 12 months	1.50	5,420	9,980
1.5 for 6 months followed by 0 for 6 months	0.75	2,510	5,130
3.0 for 4 months followed by 0.75 for 8 months	1.50	5,385	8,690

Dairy heifers were started on the indicated intake at about 3 months of age. The values are means for four to seven animals per group and have been taken from ref. (18).

Table 4

## Dietary Fluoride Tolerances for Domestic Animals

Animal	Performance (ppm F)
Beef or dairy heifers	40
Mature beef or dairy cattle	50
Finishing cattle	100
Feeder lambs	150
Breeding ewes	60
Horses	60
Finishing pigs	150
Breeding sows	150
Growing or broiler chickens	300
Laying or breeding hens	400
Turkeys	400
Growing dogs	100

The values are presented as ppm F in dietary dry matter and assume the ingestion of a soluble fluoride, such as NaF. These tolerances are levels that, on the basis of published data for that species, could be fed without clinical interference with normal performance. At lower levels of intake, some pathological changes may occur, but these changes have not been shown to influence performance. See ref. (15) for a more detailed table.

Table 5

Relationship between Fluorine Content of the Diet  
and the Development of Various Symptoms in Cattle

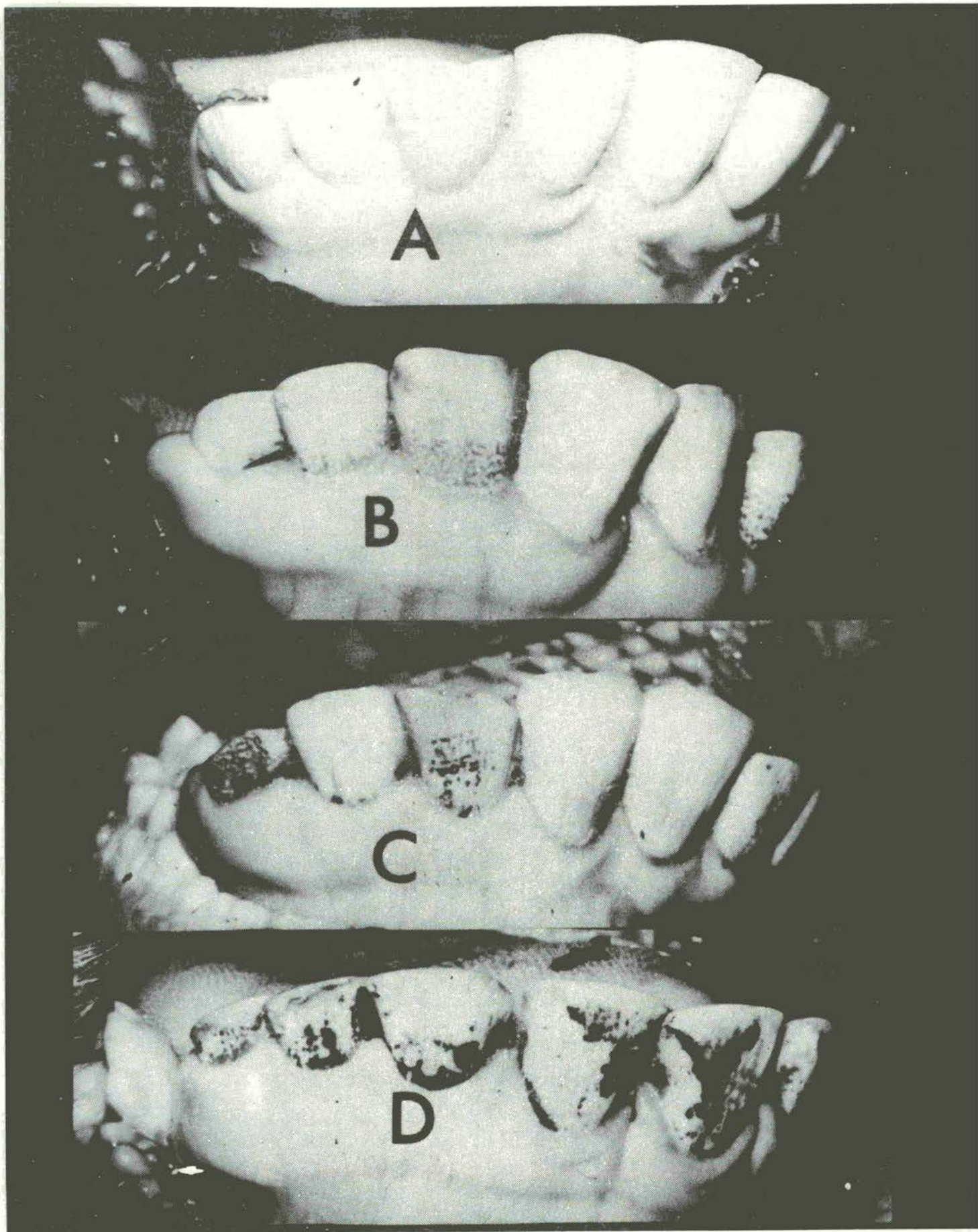
Symptom	Total Fluorine in Diet (ppm)			
	20-30	30-40	40-50	>50
Discernible dental mottling <sup>a</sup>	yes	yes	yes	yes
Enamel hypoplasia [score number (4)] <sup>a</sup>	no	no	yes	yes
Slight gross periosteal hyperostosis	no	yes	yes	yes
Moderate gross periosteal hyperostosis	no	no	yes	yes
Significant incidence of lameness	no	no	no	yes
Decreased milk production	no	no	no	yes
Skeletal F equivalent to 5000 ppm at 5 yr <sup>b</sup>	no	no	no	yes
Urine F of 25 ppm <sup>c</sup>	no	no	yes	yes

Based upon data discussed in detail in ref. (14 & 15), the statements "yes" or "no" indicate if the symptom would be reproducibly seen at this level.

<sup>a</sup>Only if fluoride is present during formative period of the tooth.

<sup>b</sup>Metacarpal or metatarsal bone, dry, fat-free basis.

<sup>c</sup>Based on values taken after 2-3 yr of exposure; specific gravity = 1.04.



1.5 mg/kg CONTINUOUS

41

3 mg / kg 4 MONTHS - 0.75 mg/kg 8 MONTHS

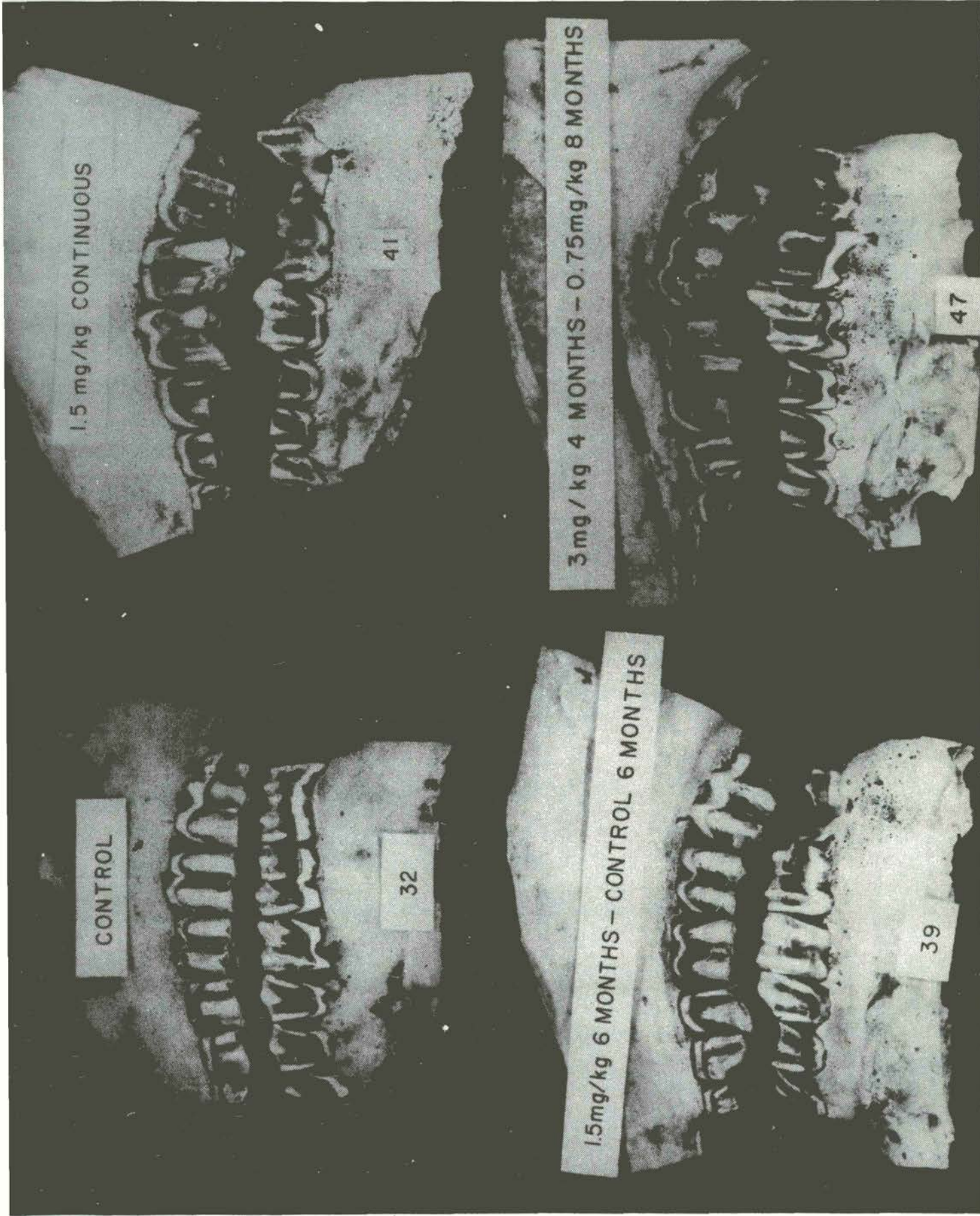
47

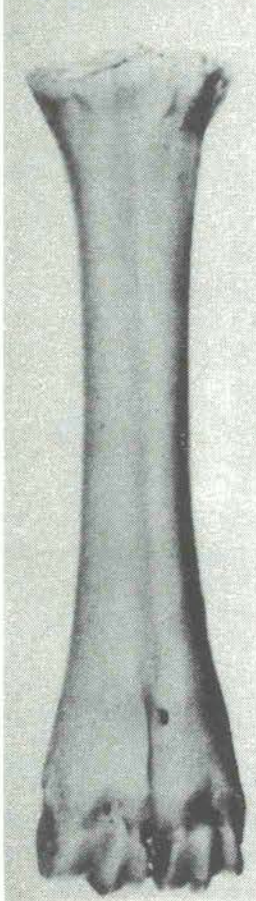
CONTROL

32

1.5 mg/kg 6 MONTHS - CONTROL 6 MONTHS

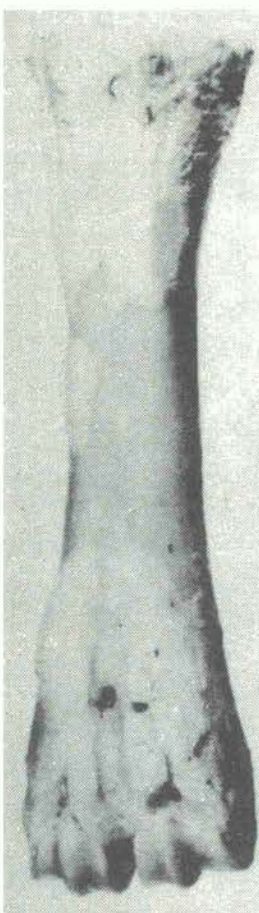
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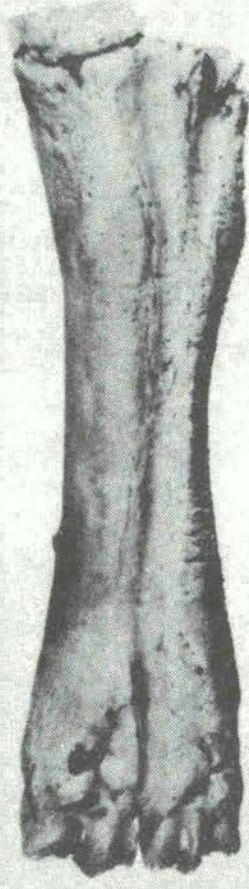
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CONTROL



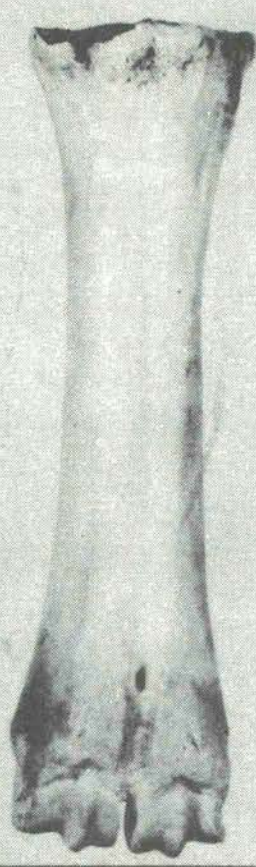
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1.5mg/kg 6 MONTHS - CONTROL 6 MONTHS



35

1.5mg/kg CONTINUOUS



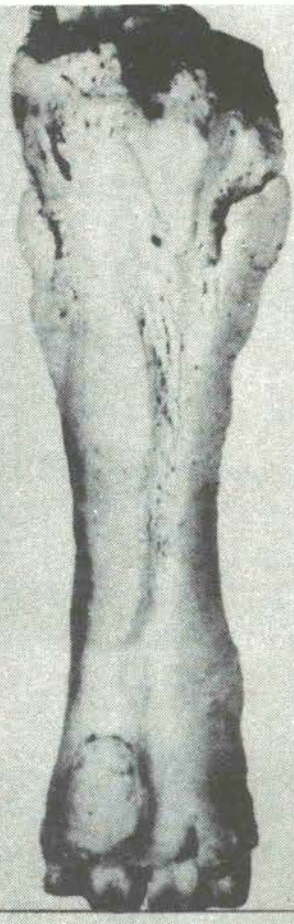
45

3mg/kg 4 MONTHS - 0.75mg/kg 8 MONTHS



41

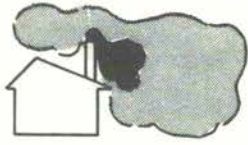
1.5 mg/kg CONTINUOUS



44

3mg/kg 4 MONTHS - 0.75mg/kg 8 MONTHS



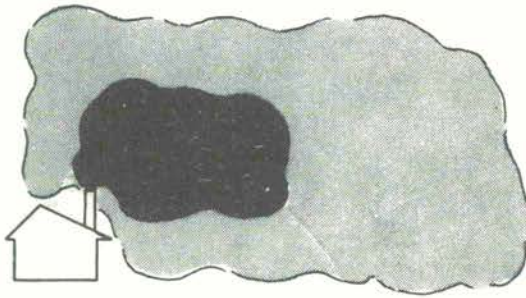


<10



70

Present Technology

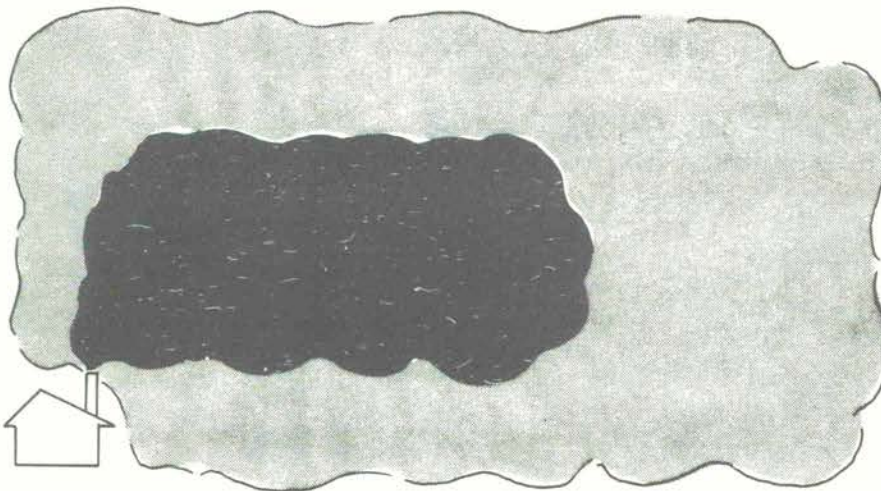


70



370

1950 - 1970



270



1040

Pre 1950 Technology



## CONCLUSIONS AND FINDINGS

### OF THE UNEP INDUSTRIAL SECTOR SEMINAR ON THE ALUMINIUM INDUSTRY

held in Paris at IBRD on 6th to 8th October, 1975

1. The seminar was attended by representatives from 17 Member governments, 30 industrial companies and 8 international organisations. A list of participants is annexed. Introductory papers, dealing with the environmental impacts associated with each stage of the production of aluminium and the questions of resources and energy involved, were presented by the Hon. W.D. RUCKELSHAUS, Professor M.C. FLEMINGS and Eng. I. NESTAAS. These papers were discussed and, subject to minor amendments, adopted by the seminar. In addition papers on "Fluoride Effects on Animals and the Aluminium Industry" and "Fluoride and Plant Life" were presented by Dr. J.W. SUTTIE and Dr. L.H. WEINSTEIN, respectively. These papers were also adopted by the seminar after examination and discussion, and along with the introductory papers formed the basis for discussion of many aspects of topics covered during the seminar.
  
2. The seminar provided an opportunity for an exchange of views among representatives of Governments, industry and international organisations. In particular attention was directed towards the following :
  - (i) examination of a number of specific issues in relation to the major environmental impacts, including those concerning workers within installations, associated with production and use of aluminium;
  - (ii) identification of trends in process developments and abatement techniques, especially for air and water pollution and solid waste disposal, to improve protection of the environment;
  - (iii) assessment of new trends occurring in and future prospects for the industry, especially in relation to management and conservation of resources, and

minimisation of demands on energy ;

- (iv) guidance to developing countries as to the best practicable means for controlling pollution.

The seminar agreed certain conclusions (see paragraphs 16 to 41), proposed a number of actions which could be taken (see paragraph 42) and established a number of areas for follow up activity by governments, industry and international organisations as appropriate ( see paragraphs 43 to 45).

## INTRODUCTION

### Aluminium supply and use

- 3. Aluminium is the most abundant metal in the earth's crust (7%) and is widely distributed throughout the world in aluminium silicates. At present bauxite is the principal raw material for production of the metal. It is used in a wide range of applications because of its low density, high strength-to-weight ratio, resistance to corrosion, high electrical conductivity, good mechanical properties at low temperature, ease of fabrication and potential recyclability with low energy requirement. There is an enormous potential for greater utilisation of aluminium especially in the fields of transportation, housing, electricity transmission and food packaging and distribution. There are advantages in substituting aluminium for some other materials, particularly where this either reduces the weight, which would allow achievement of consequent fuel savings in transportation of goods, or extends the life of a product and increases its potential of recycling, with commensurate cost and energy savings.

### Energy required in production

- 4. Considerable amounts of electrical and thermal energy are required in the production of primary aluminium although this energy required is comparable with many other metals on a per unit volume basis. Recycling of aluminium requires only a small fraction (less than 5%) of the energy used in production of the primary molten metal.

Potentially large amounts of aluminium scrap are available for recycling.

The Aluminium industry

5. The primary aluminium industry is highly integrated with a relatively small number of Companies or State Organisations throughout the world. The majority of Companies belong to the International Primary Aluminium Institute which has 51 Members with some 140 reduction works, covering approximately 80-85% of world production capacity of about 14-15 million tons per annum. Unfortunately, a considerable proportion of the remaining capacity, covered predominantly by Centrally Planned Economies, was not represented at the seminar.

Environmental impacts

6. There is a number of occupational and environmental impacts at each stage of the production process of aluminium for which both authorities and industry must apply appropriate environmental protection measures. It should be noted that it has been demonstrated possible in many places to achieve a large measure of environmental protection. These impacts may be summarised as follows :
- (a) Mining of bauxite, where the major requirements are for land restoration after mining operations, solid waste disposal, treatment of liquid effluents from ore washing, avoidance of undesirable silting, minimising dust and noise from the operation.
  - (b) Production of alumina from bauxite, which requires the disposal of the residue. This is normally done on land, but deep-sea trenches are also used where it is believed that ecological damage thereby is minimal. With land disposal attention must be given to (i) avoidance of the leaching out of highly alkaline material and contamination of ground water; (ii) control of wind blown dust and (iii) the aesthetic aspects. In some countries uses are being found for bauxite residues. Additionally, adequate dust control is required for the alumina trihydrate calcination process.
  - (c) Electrolytic reduction of alumina to aluminium gives rise essentially to air

pollution, solid waste and possibly water pollution from scrubbing effluents. The main air pollutants which must be controlled are hydrogen fluoride and particulates, although attention may also need to be paid to hydrocarbons (particularly polycyclic aromatic hydrocarbons), carbon monoxide and sulphur dioxide. The operation also involves exposure to heat and noise from which personnel must be protected. Discarded pot linings, dust and sludge from gas cleaning operations require adequate solid waste disposal and are potential sources of water pollution.

- (d) Casting, fabrication and use of aluminium products are not highly polluting activities, but may give rise to some environmental impacts due to e.g. gaseous chlorine compounds, oily effluents from washing processes, odours, acidic and alkaline effluents, as well as trace elements from chemical surface treatment, litter and solid waste. Small quantities of toxic materials may also be present.
- (e) Energy generation may give rise to air pollution from fossil fuel power and steam generation installations associated with various steps in the aluminium production process. It should be borne in mind, however, that as far as the electrical energy requirements are concerned, hydroelectric resources are often used and in the future base load nuclear sources may be increasingly used. Each have their own particular environmental impacts.

#### Effects associated with intrusions to the environment

- 7. Exposure to atmospheric fluorides and coal tar pitch volatiles particularly in the pot-room (in Söderberg plants) are conceivably the major potential health risks specific to the primary aluminium industry. In addition, working conditions are influenced by other air pollutants (sulphur dioxide, carbon monoxide and particulates) noise, heat, heavy work, risk of accidents and other factors.
- 8. **E**ffects on certain species of vegetation and grazing animals are considered to be the major potential environmental hazards outside reduction installations. Gaseous hydrogen fluoride is much more toxic to certain species of plants than

other important pollutants, such as sulphur dioxide and ozone, and can injure agricultural crops and other vegetation, giving rise to economic losses. Particulate fluorides are generally considered to be far less toxic than gaseous fluorides, but may result in increased fluoride accumulation in or on plants. High short-term exposures are generally more injurious than lower long-term exposures. The presence of other pollutants, such as sulphur oxides, may result in a greater than additive effect on plants. Animals are exposed to fluorides through the ingestion of contaminated forage, and adverse effects may be observed in cattle and other grazing animals continuously exposed to forage containing in excess of 40 ppm fluoride as annual average. No evidence has been found of significant risk to human health in populations living in the vicinity of a well operated and controlled reduction installation.

9. One effective means employed for reducing environmental impacts from residual emissions from reduction installations, especially in relation to effects on grazing animals, is the provision of buffer zones around an installation. In these areas cultivation of sensitive plants is avoided and grazing of animals is only allowed under strictly controlled conditions whereby excessive ingestion of fluorides is minimised. During the last few decades, with growing improvements in, and application of, advanced fluoride control techniques it has been possible to reduce considerably the size of buffer zones required for environmental protection, and agricultural management of these limited zones has become practicable.

#### Costs of pollution control

10. Concerning cost of pollution control two reports were used as background documents by the seminar, namely (i) " Fluoride Emission Control : Costs for New Aluminium Reduction Plants " by the Environment Committee of the International Primary Aluminium Institute (IPAI), April 1975; (ii) "Emission Control Costs in the Primary Aluminium Industry ", a study made by the United States Department of Commerce and published in " The Effects of Pollution Abatement on International Trade-III ", the Third Report of the Secretary of Commerce to the President and

Congress in Compliance with Section of the Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500), April 1975. The former report deals only with pollution control costs at new plants, and covers a wide range of techniques as applied under specific conditions. The latter report includes a first estimate of costs as applied to existing installations, but these costs are not definite and work is being continued. As shown in these reports costs of environmental control vary considerably depending on the individual installation and its location. Moreover it must be borne in mind that effective functioning of pollution control equipment will depend on a high standard of maintenance and good working relationship among staff within the plant.

11. According to the IPAI findings, typical costs can be summarised in the following manner. If it is assumed that equipment and buildings for a new aluminium reduction plant costs \$ 2 000 per metric ton of annual capacity in 1974, then the cost of fluoride emission control equipment ranges from 2% to almost 11% additional investment. The average additional investment cost is around 6,6%. There is a wide range in additional operating costs due to the emission control equipment for prebake cells from a low of \$ 6.17/metric ton of aluminium for dry primary system, to a high of \$ 52.75/metric ton for a wet primary plus a wet secondary system including a multi-purpose cryolite recovery plant. Assuming a price of about \$ 800 metric ton for aluminium ingot, this means that the additional incremental operating cost, for environmental control equipment would range from almost 0.8% to 6.6% for prebake cells.
12. At old plants, due to reasons such as structural inadequacy or insufficient space, it may be impractical or prohibitively expensive to reduce emissions to the levels possible with the latest types of control equipment. In any case the cost of retrofitting pollution abatement equipment, even at modern plant, is considered much more expensive than at new plant. Average operating costs for retrofitted equipment appear to range from about \$ 20 to 40/metric ton aluminium; but care should be taken in applying these average figures to specific installations.

### Recycling

13. Two types of waste are available as sources for recycling aluminium, and consequent savings in total energy requirements, namely "new scrap " from various processes producing and using aluminium, and "old scrap " from used fabricated products. At present most new scrap is recycled, but considerable amounts of old scrap are not. Techniques for recycling aluminium scrap once it has reached the refiner are well advanced and improving rapidly.
14. Municipal waste is a valuable potential source of old scrap but it needs to be separated. At present very little aluminium is recovered from municipal waste. Furthermore, several new municipal waste treatment processes would not allow aluminium recovery.

### Regulations

15. Different types of regulations are in force in various countries to protect environmental quality in different regions. The general principles on which many of these regulations are now based include the following, either singly or in various combinations :
  - (i) Environmental quality standards e.g. ambient air quality standards for specific air pollutants, or water quality standards which must not be exceeded. Standards are usually based on effects criteria relating to human health, aquatic impact, damage to fauna and flora or to materials, etc. ;
  - (ii) emission standards which require that emissions of specific pollutants to air or as effluents to water do not exceed certain values. They can be defined in terms of total emissions per unit of output (a standard directed towards the quality of the control equipment) or per unit of time ( a standard directed towards the quality of environmental control) ;
  - (iii) requirements based on use of particular types of control techniques where the average design efficiency has been established, but leaving the selection of



specific techniques to the installation in question.;

- (iv) zoning regulations, concerning for example the location and size of a plant, the size of a buffer zone and the standards to be met at the property line, etc.;
- (v) procedures by which authorities negotiate with individual plants the best practicable means for protecting the environment under the specific circumstances of that particular plant. This procedure usually incorporates a compulsory inspection and may require the plant to monitor its emissions or effluents;
- (iv) direct contractual agreement between authorities and a company concerning environmental protection measures to be taken and a time table for implementing them.

## CONCLUSIONS

### (a) Approach to pollution control

16. The seminar recognised that the Industry, in general, has made and will continue to make considerable progress in both application of environmental protection measures and in development of improved cost-effectiveness abatement techniques. Industry accepts that emissions should be held at levels which do not harm either the health or welfare of the workers within a plant or the surrounding environment. In the industrialised countries total emissions of fluorine compounds, for example, from primary aluminium smelting have been decreasing in recent years, despite increasing production capacity. The industry has also been very active in resource management, implementing techniques which reduce the total energy needs and developing new process technologies. Bearing in mind that pollution problems from the aluminium industry are essentially at the local level and the particular intrusions on the environment vary from plant to plant depending on size of plant and local conditions, it is recognised that much still remains to be done in the future.
17. Industry is an important source of technical innovation and management. It has

accepted the desirability in the long term to move from the present situation of add-on pollution abatement to a new comprehensive, integrated approach with low energy, low polluting technologies. However, it is appreciated that the speed at which this process can take place is determined by many external factors and it may be a long time before such an integrated approach can be attained. Meanwhile, there may be important trade-offs to be assessed in terms of wise use of resources whether those be material, economic, energy or environmental. It is recognised that a contribution to this process may be made through effective cooperation amongst governments, industry, universities and the scientific and technical communities.

18. The advanced industrialised nations and the industry further recognise a responsibility to those developing countries in various stages of industrial development, and the need for effective transfer of technical know-how and experience. A high standard of production technology and control equipment is available commercially for countries willing to utilise this know-how and experience.

(b) Criteria for identification of problems

19. The seminar has not attempted to make an assessment and definitive evaluation, but rather to identify the broad environmental problems involved in relation to the aluminium industry and the appropriate techniques for dealing with these problems. Specific government policies and particular solutions applied at individual plants are not considered to be within the mandate of the seminar. However, four criteria have been identified which are used in establishing and implementing policies namely :
  - (i) the need to assess the risks to health and welfare and to the environment of the broad spectrum of intrusions into the environment arising from aluminium production and use ;
  - (ii) the need to assess the benefits of control of intrusions into the environment;
  - (iii) the need to assess the total costs in the broadest terms including not only

abatement techniques but also socio-economic aspects and energy requirements;

(iv) the need to assess the rate of implementation of actions and to foresee an adequate time-table in full cooperation between environmental protection authorities and industry, taking full account of public interests.

20. Some countries recognise the need to consider installation of pollution control equipment on a plant by plant basis when licensing the construction and operation of a new plant; whilst others require uniform application of certain levels of control. In view of the additional expense of retrofitting it is emphasised that long term pollution control planning is essential. This should be done in cooperation with industry, which should have confidence that its investments in environmental protection may be economically viable over the life time of the equipment. It was further noted that in some countries contractual arrangements to this end are made between governments and industry.

(c) Prospects concerning improvement in pollution control

21. It is fully accepted that pre-siting surveys and environmental impact assessment should be made by industry and approved by the environmental protection authority before construction of a plant is authorised. Operating conditions should be defined, as they affect the environment, based on the environmental impact assessment. Again such plants should be considered on an individual basis taking all local physical and social conditions into consideration.

22. Concerning the disposal of bauxite residues adequate technologies are available for impounding on land without loss of material or discharge of alkaline effluent. It is essential, however, to take into account the physical characteristics of the bauxite as well as the local weather conditions in designing new disposal ponds, and the visual amenity in choosing the location of ponds. These areas may be re-vegetated after a period of time.

23. Improvements could be made in respect of operating existing processes through the use of automatic equipment, especially at reduction plants, which would

reduce emissions and improve working conditions. Improvements should also be made, as appropriate, in the ventilation systems and primary exhaust systems of the pot-room to ameliorate conditions for employees in the plant. Fume generation and losses in the recovery processes could be reduced by improved techniques.

24. Sea water has a high fluoride and sulphate content as well as a high buffering capacity, and thus sea water pollution by fluorides from aluminium production is not a problem. On the other hand the fluoride and sulphate content of drinking water has to be controlled. In relation to water pollution in general attention should also now be directed towards other pollutants e.g. grease and soluble hydrocarbons, cyanides, trace toxic elements and phenols, not only from scrubbing liquors at the reduction plants, but also from anode baking and foundries.

(d) Working conditions

25. Extensive investigations indicate that exposure to work atmospheres containing fluorides is not a significant health risk under normal operating conditions. As a safety precaution, the fluoride content of the urine of the pot-room personnel should be monitored. Further, respiratory irritation and additional or synergistic effects of dust and gases (hydrogen fluoride, sulphur oxides, carbon monoxide, hydrocarbons, etc) should be investigated. There is a possibility of coal tar pitch volatiles (certain polycyclic aromatic hydrocarbons) causing cancer after long time exposure, a possible problem now subject to extensive research in several countries.
26. Existing standards for composition of the working atmosphere seem adequate to protect the health of people. Future developments may however show that more strict standards are needed. In any case monitoring of the working environment and of exposure of individuals, as well as medical examinations should be carried out on a routine basis.
27. To promote the health and well-being of people working in the plants, present efforts to reduce accidents and exposure to fumes, heat and noise should be

continued and extended. Workers should participate in the planning and implementation of occupational health and safety programmes. Application of the principles of ergonomics is essential to improve working conditions. When new equipment or processes are developed, due consideration should be given to relevant occupational safety and health standards, to ergonomic design, as well as the health and welfare of the workers in a plant.

28. The seminar noted that there has been good co-operation amongst IPAI members, ILO and WHO on occupational health issues and stressed the importance that present efforts to this end should be extended.

(e) Future trends with respect to the aluminium industry

29. Throughout the seminar a number of important future trends with respect to the aluminium industry were identified. These trends fall into three categories, namely :

- (a) new process technologies and control techniques for all stages in the industry;
- (b) new energy saving processes and techniques both for primary aluminium production, casting and fabricating;
- (c) increased possibilities for recycling.

Additionally, it was noted that an increased use of aluminium may result in substantial energy savings in certain sectors e.g. transportation and the motor vehicle, power transmission and household construction.

30. A number of factors were recognised which affect the aluminium industry and will accelerate modernisation and replacement of obsolete air polluting plants. These include : (i) rising energy costs; (ii) more stringent control regulations; (iii) the need to improve the working environment; (iv) new process technologies.

(f) New process technologies

31. A number of new processes technologies are under development, both in respect of the Bayer alumina production process and the Hall-Heroult electrolytic reduction

process, which could reduce the overall energy needs in the production of aluminium and may reduce the environmental impact potential. It is not foreseen, however, that the cost advantages and improvements to be obtained from these new processes will bring about a rapid change in the utilisation of the conventional processes. The reasons for this are two fold. First, these new processes have not yet been proven on an industrial scale. Second, considerable capital would be required to convert conventional processes to these new processes. Consequently a relatively long lead time may be anticipated for their wide scale introduction.

(g) Energy

32. Much progress has been made in recent years by the aluminium industry to reduce energy consumption. A major area for energy reduction in the long term is in the smelting process, and processes such as the chloride "closed loop " process which shows promise of reducing pollution as well as energy consumption. Reduction in energy consumption using this process may be as much as 30%.
33. In the shorter and intermediate term, a major opportunity exists for reducing energy consumption in the melting, casting and fabricating areas. Improved technology such as special electric melting furnaces shows great promise. Introduction of computer scheduling has been of great help. In general, energy savings are possible through (a) improved management practices, (b) introduction of improvements and existing technology at plants and (c) development and introduction of new technology. Energy is the largest single component in production costs for aluminium. Energy has now passed labour as a production cost in many fabricating plants.

(h) Prospects for further recycling

34. In view of the enormous energy savings involved it is important that much more aluminium (both new and old scrap) is recovered and recycled. In general, the technology in relation to recycling old scrap is improving rapidly . Areas where further technological developments are required include (a) collection and segregation of alloys and refining ; (b) recycling of composite materials themselves;

(c) removal of contaminants from dross and its reuse. Note should be taken that some problems of recycling are multi-industrial and not only associated with the aluminium industry. Any activities to improve recycling of aluminium will affect a number of other industries and vice versa. Recycling would be easier with structural changes in fabricated products containing aluminium, both in terms of amount of aluminium and its association with other materials. Finally, it should be noted that improved statistical data concerning scrap would enable a better assessment of the benefits and costs of recycling.

35. Municipal waste is recognised by the industry as a potential source of aluminium scrap which could be recycled to augment the supply of aluminium. There is increasing interest in recycling municipal waste in view of (i) the value of the materials and energy contained therein; (ii) the difficulties in finding suitable waste disposal sites; (iii) the increasing severity of air and water pollution regulations; and (iv) the increasing costs and large energy requirements involved in the production of primary aluminium. More effective means are required for economic collection of municipal waste and separation of aluminium. Much more could be done to educate and inform the public concerning this question.

(i) Resources

36. In respect of the aluminium industry the major resources are : (i) energy ; (ii) raw- materials (both bauxitic and non-bauxitic) ; (iii) capital ; (iv) human resources (both skilled and managerial ) ; (v) infrastructure. Large amounts of bauxite reserves exist in the world but non-bauxitic sources of aluminium will eventually be used. It is doubtful whether there will ever be a shortage of raw materials for aluminium production.
37. Two dichotomous trends related to resources are observable in respect of siting of new plants. One is to site them near the supply of raw materials and hydro-electric energy. The other is to site them in the industrialised regions of the world with the infrastructure and near skilled labour and the markets . The former frequently means in remote areas as well as in developing countries. The latter

also has the advantage of being able at times to integrate aluminium production with fabrication avoiding the energy of remelting as it is usually more expensive to transport fabricated goods than the metal. In both cases, and even where stringent emissions limits have been imposed, careful site choice, good engineering practice and design of pollution control equipment have given freedom in location whilst meeting the required environmental protection standards. Consideration will continue to be given to siting of plants particularly in countries which possess large amounts of unused hydroelectric power or other relatively inexpensive fuels e.g. flare gas.

(j) Capital

8. Shortage of capital may well prove a greater constraint on development of the aluminium industry and on advances in materials recovery than technology. The shortage of capital is evident in all industrial sectors throughout the industrialised world. It is estimated by numerous authorities that it will amount to over a trillion dollars in the decade ahead and will particularly affect such a heavily capital intensive sector as aluminium.

(k) Possible repercussions in trade

9. There are potential repercussions on trade patterns which might arise through widely different pollution control requirements. The costs of pollution control vary considerably between plants depending on different processes, age of plant, locations, regulations, etc. Requirements to up-grade pollution control equipment at existing plants and especially plants with no controls can give rise to a significant economic impact on an individual plant. However, one case is likely to differ from another. Based on model calculations, it can be estimated that the installed costs of air pollution control at new primary aluminium smelting plant range from 5 to 10% of the total costs of the plant; operating costs vary from 1 to 5% of the sales price of aluminium. In as much as local variation in the price of power, cost of labour and transportation are as important if not of greater impact, it is



not considered that for a large company as a whole that significant trade distortions are likely; although the costs of pollution control may, in selective circumstances, have significant impact on the profits from an individual plant. This could particularly affect small companies with few plants.

(l) Monitoring

40. In addition to establishing standards for emissions from smelters, one integral part of any system of environmental control must be monitoring, both of emissions to air and water, where this is possible, and of their environmental impact within the vicinity of the smelter. Monitoring of emissions will indicate whether the standards for such emissions are being met; if not, results of monitoring will alert industry to the need for suitable corrective action. Monitoring of the environment can include assessing ambient concentrations of fluorides and measurement of the accumulation of fluorides by vegetation and by cattle. This should enable both industry and government to assess whether the desired degree of protection against the effects of fluorides is being achieved and will again enable corrective actions to be planned and taken if necessary. Measurement should also be made of pollution effluents to water. Ideally, monitoring should commence before a smelter is on line in order to have base line data against which future data can be assessed. Equally, it is very desirable that both government and industry should be involved in such monitoring; this ensuring that there be mutual acceptance of the results of monitoring, and helping facilitate rapid collective actions to be taken if monitoring results are unsatisfactory, preferably without the necessity of involving formal legal procedures. Internationally comparable methods of monitoring and measurement should be established within the industry; and results of measurements should be expressed in metric units.

(m) Developing countries

41. Although, unfortunately, very few participants from developing countries took part in the seminar, there was general appreciation of the aspirations of developing countries for industrialisation and their needs for environmental guidance. It was agreed that the aluminium industry should be encouraged to invest in developing

countries which have the required resources. Developed countries have already demonstrated their willingness to share their environmental experience with developing countries and suitable mechanisms must now be found for encouraging transfer of technology and dissemination of knowledge as to best practicable means for controlling pollution.

#### ACTIONS PROPOSED

42. Participants at the seminar agreed that the following actions should be taken :
- (a) In assessing the level of control needed under specific environmental conditions, environmental protection authorities in countries should take full account of the external environment of the plant as well as all aspects of the working environment. Consideration should be given in setting regulations to the avoidance of the transfer of pollution problems from one medium to another and from the working to the external environment and vice-versa;
  - (b) Pollution control techniques are available and should, where necessary, continue to be developed and increasingly applied at a number of steps in the production of aluminium. In particular the following sources of pollution should be considered for control :
    - (i) liquid effluents from deposits of bauxite residues on land;
    - (ii) emissions from aluminium oxide calciners ;
    - (iii) emission of airborne fluorides from primary reduction ;
    - (iv) emission of tar pitch volatiles and fluorides from anode baking facilities;
    - (v) discharge of scrubbing liquors and other effluents from primary reduction, fabricating and the secondary industry, due consideration being given to the properties and uses of the receiving waters.
  - (c) Further technological developments should be made in the area of pollution control, as well as better problem definition, in addition to those areas

mentioned in (b) above, for the following :

- (i) control of emissions of sulphur oxides, carbon monoxide, tar pitch volatiles and dust from primary aluminium production;
  - (ii) noise at several steps in the production process ;
  - (iii) economic uses of bauxite residues.
- (d) Means should be provided at all plants for collecting pot gases ; all plants should have primary exhaust. In cases where the most advanced pollution control equipment is not applied initially, consideration should be given to the provision of adequate space and strength of structures so that improved cleaning equipment may be added later, if and when required.
- (e) In selecting favourable sites for reduction plants surveys should be required which identify and describe important features of the area such as topography, meteorology, indigenous and cultivated vegetation. Both ambient air, water and forage sampling programmes in the vicinity of the plant should be carried out both before and after construction and operation. Emphasis should be placed on fluorides in the atmosphere and natural waters, and, that which accumulates in forage, aquatic biota and in the bones of herbivores. Where necessary, or desirable, other pollutants may be monitored. The condition of vegetation should also be assessed periodically. There should also be requirements to monitor the working environment and exposure of personnel. All sampling and analytical methods should be standardised on an international basis. Pre-siting plant surveys should not unnecessarily delay construction of a plant.
- (f) Provisions should be agreed between authorities and industry with respect to emergency actions to be taken if plant and control equipment are not functioning properly.
- (g) Bearing in mind that presently there may be different trade-offs between

low energy consumption and polluting control, unless there are overriding considerations, incentives should be given to industry in the development and application of lower energy-consuming, lower pollution potential technologies for the production of aluminium. An environmental impact assessment should be made of new technologies before they are allowed to be installed on a wide scale. Research and development into ways of using waste products should be encouraged.

- (h) Fabricated aluminium products should be designed with at least the following two criteria : (i) long life and durability; (ii) recyclability minimising composite materials which do not allow this. Authorities and industry should find ways and means to promote recycling of fabricated products in a cost-efficient manner.
- (i) Industry, governmental financial sponsors and financing institutions, when investing in developing countries, should be encouraged to ensure that the technology transferred incorporates the best appropriate environmental practice for the site.
- (j) Every encouragement should be given to close cooperation between government and industry in the long term planning of policies and agreement of suitable time-tables for policy implementation
- (k) It is recognised that governments, industries, universities and the wider scientific and technical communities all have contributions to make to areas of energy and resource conservation and to environmental aspects of aluminium production, and improved ways should be found to foster this interaction.

#### POSSIBLE FOLLOW-UP ACTIVITIES

- 43. It is proposed that a number of follow-up activities to the seminar should be undertaken, singly or jointly, as appropriate by (i) governments; (ii) industry

and (iii) the UNEP, in cooperation with other UN agencies and other international organisations as follows :

- (a) Guidelines should be designed, especially for the benefit of developing countries and countries new to the industry, for siting criteria and systems of control for environmental impact for those processes where the aluminium industry makes a particular intrusion into the environment.
- (b) Where not already available, the cost-effectiveness of proven pollution control techniques for the environmental intrusions arising from the major processes in production of aluminium should be evaluated, at intervals appropriate to the rate of technological change and the investment pattern of the industry.
- (c) The IPAI comprehensive surveys of current national legislation and regulations should be extended to cover all stages of primary aluminium production and continue work of developing a glossary of terms.
- (d) The techniques for measurement of emissions or intrusions into the environment should be established on an internationally comparable basis for the main stages of aluminium production, so that progress in implementing abatement may be measured in relation to those problems which exist in the aluminium industry and in the context of similar emissions from other industries.
- (e) Additional data should be collected and criteria established in relation to exposure of human beings, aquatic life, fauna and flora for all the major emissions from aluminium production, including noise.
- (f) Cost evaluations should be made of new technologies as they are developed, and of the control of relevant environmental impacts.
- (g) An evaluation should be made of ways and means to conserve both energy and resources through improved processing techniques and improved recycling.

- (h) Improved methods should be found to foster interaction on technical and environmental problems among industry, governments, universities and the broader technical and scientific communities.
- (i) A dialogue should be encouraged between industry, governments and the public in order to establish good environmental resource management procedures in relation to aluminium production and use e.g. in setting standards, assessing environmental control levels required, incentives for investing in control equipment and its proper functioning, etc.

44. In view of the multi-industrial aspects involved in effective recycling of industrial and municipal waste, an exploratory meeting of experts should be held to consider the possibilities of organising a seminar to examine the problems and issues involved in more wide spread application of recycling in a cost-effective manner.

45. Finally, a mechanism should be established within UNFPA for regular reporting by industry, governments and relevant intergovernmental organisations of progress made in implementing the actions proposed by this seminar. It is suggested that statements should be biennial, completed not later than the end of December of the reporting period and with a first report in December 1977. These reports should be circulated to all interested parties.

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U.N.E.P.

Industry Programme

ALUMINIUM SEMINAR  
Paris, 6-7-8 October 1975

LIST OF PARTICIPANTS

ALTENPOHL, Dieter      Director of Technology, Swiss Aluminium Ltd.  
Feldeggstrasse 4, PO Box 495, 8034 ZURICH,  
Switzerland

ATKINS, P.R.            Manager, Environmental Control  
Aluminum Company of America  
Alcoa Building, PITTSBURGH, Pennsylvania 15219,  
U.S.A.

BALTENSPERGER, Karl    Technical Manager, Aluminium Bahrain  
PO Box 570, BAHRAIN, Arabian Gulf

BENARD, Francois      Adjoint au Directeur-Aluminium Pechiney  
29, rue de Chateaubriand -75008 PARIS- France

BENSCH, H.             Manager, Vereinigte Aluminium-Werke Adt.  
Gerichtsweg 48, PO Box 626, 53 BONN  
Federal Republic of Germany

BERNHEIM                Secrétaire, Groupe Aluminium  
Comité de Liaison des Industries de métaux  
non-ferreux  
Commission des Communautés Européennes  
12 Boulevard de Berlaimont, 1000 BRUXELLES,  
Belgium

BERRY, R.P.L.          Chairman, Alcoa of Great Britain Ltd.  
PO Box 15, ALCOA House Corbett Avenue,  
DROITWICH, United Kingdom

BOHM, E                 Luigi-Chemie und Huttentechnik GmbH.  
Gervinins Str. 13/15 D-6000 FRANKFURT AM MAIN  
Federal Republic of Germany

BONNET, P.              Administrateur Principal, Service de  
l'Environnement et de la Protection des  
Consommateurs  
Commission des Communautés Européennes  
Rue de la Loi 200, 1040 BRUXELLES, Belgium

BROCKE, Prof. Bismarck Platz 1  
1, BERLIN 33

BUTLER, R.F. Executive Aide, President's Staff  
Reynolds Metals Company  
Reynolds Metals Building, RICHMOND  
Virginia 23261 - U.S.A.

CHANG TIEN-YIN Chinese Society of Metals  
May 4th Rd. PEKIN  
Peoples Republic of CHINA

CHEN TAI Chinese Society of Metals  
May 4th Rd. PEKIN  
Peoples Republic of CHINA

COOK, Peter B. Aluminium Bahrain  
PO Box 570, BAHRAIN, Arabian Gulf

COPPEE, Georges Occupational Safety and Health Branch, I.L.O.  
1211 GENEVE 22, Switzerland

COULON, Jean-Pierre Director du Service Médical,  
Péchiney-Ugine-Kuhlmann  
23, rue Balzac, 75008 PARIS, France

CYWIN, Allen Director, Effluents Guidelines Division  
Environmental Protection Agency,  
WASHINGTON D.C. 20460 - U.S.A.

DENNISON, Charles S. Senior Advisor, U.N.E.P.  
485 Lexington Avenue,  
NEW YORK, N.Y. 10017, U.S.A.

DIETHRICH, Robert Président du groupe de travail sur  
l'aluminium à l'O.C.D.E.  
Chargé des affaires internationales et des  
questions commerciales, Ministère de  
l'Industrie et de la Recherche  
99, rue de Grenelle, 75700 PARIS, France

DINMAN, B.D. Medical Director, Aluminium Company of America  
Alcoa Building, PITTSBURGH, Pennsylvania  
15219, U.S.A.

DOBOS, G. Deputy Director, Industrial Policies &  
Programming Division - U.N.I.D.O.  
PO Box 707, 1011 VIENNA, Austria

DOYLE, J. Attorney at Law, Reynolds Metals Company,  
Reynolds Metals Building, RICHMOND,  
Virginia 23261 - U.S.A.



EDWARDS, Bruce R.      Coordinator of Environmental Control  
Raw Materials and Smelter Division  
Aluminum Co. of Canada  
Box 6090, MONTREAL 101, Quebec, Canada

ELTON, P.J.              Chairman, Alcan (U.K.) Limited  
Alcan House, 30 Berkeley Square,  
LONDON W1X 6DP, U.K.

FAUVEL, Renee          Principal Administrator, Directorate for Science,  
Technology and Industry, O.E.C.D.  
2, rue Andre Pascal, 75775 PARIS Cedex 16,  
France

FLEMINGS, Merton C.    Ford Professor of Engineering,  
Massachusetts Institute of Technology,  
CAMBRIDGE, Massachusetts 02139, U.S.A.

GRAHAM, Peter John     Principal, Industrial and Commercial  
Policy Division  
Department of Industry  
1, Victoria Street, LONDON S.W.1.

GUINARD, Charles       Directeur du Marketing - Aluminium Pêchiney  
29, rue de Chateaubrand, 75008 PARIS, France

GUTHE, T.                Medical Director, Elkem-Spigerverket a/s  
Middelthuns gate 27, PO Box 5430, OSLO 3, Norway

HAINES, John            Principal Administrator, Environment Directorate  
O.E.C.D., 2 rue André Pascal, 75775 PARIS Cedex 16,  
France

HAMADA, Takao          Chief Environmental Engineer,  
Nippon Light Metal Co. Ltd.  
7-3-5-Chome, Ginza, Chuo-Ku, TOKYO, Japan

HARRIS, John            Technical Adviser, U.N.D.E.S.A.  
U.N. Building, NEW YORK, N.Y. 10017, U.S.A.

HUGHES, James P.        Medical Director,  
Kaiser Aluminium and Chemical Corporation,  
300 Lakeside Drive, OAKLAND, California 94604,  
U.S.A.

ISMAIL, Youssef        Chairman, The Egyptian Aluminium Smelter  
5 Emad El Din Street, CAIRO, Egypt

JANCZAK, Jacek          Environment & Human Settlements Division,  
Economic Commission for Europe,  
Palais des Nations, CH1211 GENEVE, Switzerland

JOHNSON, M.D.C. Assistant Secretary, Minerals, Metals, Electrical Engineering - Process Plant, Industrial Technology Division, Department of Industry, Millbank Tower, Millbank, LONDON S.W.1. U.K.

JOHNSON, S. Chef de la Division de l'Environnement et de la Protection des Consommateurs, Commission des Communautés Européennes Rue de la Loi 200, 1040 BRUXELLES, Belgium

JOUVEN, Pierre Président d'Honneur, Péchiney-Ugine-Kuhlmann, 23, rue Balsac, 75008 PARIS, France

KOLLONTAI, Vladimir Chief of Planning and Policy Section Research Division, UNCTAD, Palais des Nations, GENEVE 10

LEDER, L. Kaiser Prussag Aluminium G.m.b.H. & Co. Voerde 4223 VOERDE, Postfach 100, Federal Republic of Germany

LEE, Bong Chool President, Aluminium of Korea, Ltd. C.P.O. Box 4857, SEOUL, Korea

LEMAHIEU, J.M. Ingénieur, Chargé du Secteur électrométallurgie Ministère de l'Industrie et de la Recherche 99, rue de Grenelle, 75700 PARIS, France

LEMMON, W. Chief, Mining, Mineral & Metallurgical Division, Environmental Protection Service, Canadian Department of Environment, OTTAWA, Ontario

LESTER, Murray D. Manager, Aluminium Company of Canada Ltd., Box 6090, MONTREAL 101, Quebec, Canada

LEUTERT, G. Chef, Section Industrie et Artisanat, Office Fédéral de la Protection de l'Environnement, CH 3003 BERNE, Switzerland

MacDONALD, Administrator Industrial Structures Division O.C.D.E. 2, Rue Andre Pascal, 75775 PARIS Cedex 16, France

MacGREGOR, Ian Chairman, Amax Inc. Amax Center, GREENWICH, Conn. 06830, U.S.A.

MARTYN, Peter Secretary General, International Primary Aluminium Institute, New Zealand House, 9th Floor, Haymarket, LONDON SW1Y 4TQ, U.K.

MENEGOZ, Charles D. Chef du Service Antipollution de la Division  
Aluminium Pechiney-Ugine-Kuhlmann,  
23, rue de Balzac, 75008 PARIS, France

MOENICH, D.M. President, Apex International Alloys Inc.  
2340 Ave. Des Plaines, Illinois 60018, U.S.A.

MOORHOUSE, James Manager, the Rio Tinto-Zinc Corporation  
6, St. James, s Square, LONDON SW1Y 4LD, U.K.

NESTAAS, Ivar Engineer, I/S Miljøplan  
Maries Vei, 20, 1322 HØVIK, Norway

OOSTERHUIS, O. Vice-Président, Hunter Douglas N.V.  
2 Piekstraat, PO Box 5072,  
ROTTERDAM, Netherlands

OSTRANDER, F. Taylor Assistant to Chairman,  
Amax Inc., Amax Centre, GREENWICH, Conn. 06830,  
U.S.A.

POTIER, Michel Head, Division Central Analysis & Evaluation Unit,  
Environment Directorate, O.E.C.D.,  
2, rue Andre Pascal, 75775 PARIS Cedex 16, France

QUAGLIA, Mario E. Secretaria Ambiente Humano  
25 de Mayo, BUENOS AIRES, Argentina

REDOUX, Alain Ingénieur EMSTA, Service des Problèmes de  
l'Atmosphère  
Ministère de la Qualité de la Vie,  
Environnement  
14, Bld. du Général Leclerc, 92521 NEUILLY  
France

REEF, Arthur Chairman, Advisory Committee  
Center for International Environment  
Information,  
Carnegie Institute, 436 E. 46 Street,  
NEW YORK, U.S.A.

ROLLER, H. Manager, Alcan Australia Limited  
PO Box 1, KURRI KURRI N.S.W. 2327, Australia

de ROSEN, Leon Director, Industry Programme U.N.E.P.  
17, rue Margueritte, 75017 PARIS, France

RUCKELSHAUS, William D. Attorney at Law, 1 Farragut Square South,  
WASHINGTON D.C. 20006, U.S.A.

SAHER. Ibrahim           Assistant Professor, Academy of Scientific  
Research and Technology  
CAIRO, Egypt

SATAPATHY, S.            Chief of Technology,  
Bharat Aluminium Company Ltd.,  
Korba Aluminium Project, P.O. Balco Township,  
Korba Pin Code No. 495684,  
DISTT. BILASPUR (M.P.), India

SATO, Junichi            Assistant Manager, Division of Research &  
Development  
Department of Technology, Chiba Factory,  
Showa Denkoh Co. Ltd., 3 Yahatakaigandori,  
Ichihara-Shi, CHIBA - Pref. Japan

SERPETTE, Maurice        Directeur Général, Pêchiney-Ugine-Kuhlmann  
23, rue Balsac, 75008 PARIS, France

SHELDON, Allen C.       Vice President, Aluminium Company of America,  
Alcoa Building PITTSBURG, Pennsylvania 15219,  
U.S.A.

SHIM, W.J.              Assistant of the President of Aluminium  
of KOREA  
SEOUL - KOREA

SOLHJELL, Svein         Ingénieur, Directeur de l'Organisme National  
pour le Contrôle de la pollution,  
OSLO 1, Norway - Postboks 8100 -

SMITH, W.R.             Manager,  
Kaiser Aluminium and Chemical Corporation  
300 Lakeside Drive, OAKLAND, California 94604,  
U.S.A.

STROHL                  Pêchiney-Ugine-Kuhlmann  
16, rue de Monceau - 75008 PARIS, France

STRONG, Maurice F.      Executive Director, U.N.E.P.,  
PO Box 30552, NAIROBI, Kenya

SUTTIE, J.W.            Professor of Biochemistry,  
University of Wisconsin,  
MADISON, Wisconsin, U.S.A.

TSIEN YU CHIEH         Chinese Society of Metals  
May 4th Road, PEKIN  
Peoples Republic of CHINA

TIXHON, Jean            Office of Environmental & Health Affairs,  
I.B.R.D., 1818 H. Street, N.W. WASHINGTON D.C.  
20433, U.S.A.

TROVO, Antonio G.      Chef du Service Antipollution et sécurité-  
Alumetal SpA.,  
Via Alserio 22, 20159 MILANO, Italy

UTIGER, R.E.            Managing Director,  
The British Aluminium Company Ltd.,  
Norfolk House, St. James's Square,  
LONDON SW1Y 4JS, U.K.

VAUTREY, J.P.          Adjoint au Chargé des Affaires Internationales  
et des questions commerciales, Ministère de  
l'Industrie et de la Recherche,  
99, rue de Grenelle, 75700 PARIS, France

VESSERON, Philippe    Ingénieur des Mines, Service des Problèmes  
de l'Atmosphère  
Ministère de la Qualité de la Vie, Environnement  
14, Boulevard du Général Leclerc,  
92521 NEUILLY, France

WAENERLUND, Göran    Vice-President Smelting, Gränges Aluminium AB  
Fack, 85101 SUNDSVALL 1, Sweden

WEINSTEIN Leonard H.   Programme Director, Environmental Biology,  
Boyce Thompson Institute for Plant Research,  
YONKERS, N.Y., U.S.A.

WESENBERG, Harald    Chief Research Officer,  
A/S Ardal og Sunndal Verk  
Sorkedalsveien 6, PO Box 5177, OSLO 3, Norway

WILDSCHULTZ, W.F.    European Primary Aluminium Association  
P.O. Box 1207, Königsallee 30,  
D-400 DUSSELDORF 1,  
Federal Republic of Germany

OBSERVERS

BRANDI, F. Member Organisation, I.C.I.E.  
Federation of German Industries

COCHRANE, C.A. Chief Executive,  
International Centre for Industry and the  
Environment (I.C.I.E.)  
PO Box 30643, NAIROBI, Kenya

CUSELL, F. Member Organisation I.C.I.E.  
Federation of Netherlands Industries

DE LA CALLE, P. International Centre for Industry  
and the Environment

FEATHERSTONE, J.W. Member Organisation I.C.I.E.

FENEON, R.K. Member Organisation I.C.I.E.  
International Chamber of Commerce

GENY, Pierre Member Organisation I.C.I.E.  
International Iron and Steel Institute

GLADWIN, T. C.E.I.M.

GOFFI, M. Banque Européenne d'Investissement

RESS, Paul U.N.E.P., Attaché de Presse

RISSELADA, T.F. International Petroleum Industry Environment

ROYSTON, M. C.E.I.M.

SEDLACEK, K.W. Conservation Association (IPIECA)