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TSSCIT

Technology of stabilisation and solidification of contaminated mercury chlor-alkali waste with sulfur microcements

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TSSCIT TECHNOLOGY

The TSSCIT "The Stabilization and Solidification CIT Technology " is a cement based technology to treat contaminated soils or wastes .
Even wastes coming form others remediation process, as it ºmight be thermal desorption, as a final treatment of the wastes.
It consists in the following steps :

1º- Study of the contamination components .
2º- Study of the matrix.
3º. Select the appropiate cements , admitures and complementary materials.
4º. Select the properties of the final material and look for the optimum formulation
5º- Select the process of mixing and curing.
6º- Chemical and Physical Tests.
7º- Field Trial and Industrial Project.

1º- Study of the contamination components .

This first step consists in the analysis of the contaminated chemical compounds in the soil or waste to treat and its quantification.

The mercury forms present in the wastes and demolition materials of Mercury Chlor-Alkali Plants are :

- Metallic mercury
- Solid mercury compounds , specially HgO
- Dissolved mercury, essentially present as : $[HgCl_4]^{2-}$

1º- Study of the contamination components .

In the Project for early ratification and implementation of the Convention of Minamata in Uruguay, we studied with this TSSCIT "Stabilization and Solidification CIT Technology " the treatment of two industrial wastes of the Mercury Chlor-Alkali Plants of the Efice Uruguay Company:

Masa desmercurizante

Barros de Salmuera

With a content of total mercury as :

	%Hg
Masa Desmercurizante	6,5
Barros de Salmuera	0,2

2º- Study of the matrix.

Our target with this microcements technology are soils and wastes with small amounts of contaminants, in which the matrix is the predominant material.

This matrix usually contains materials that are incompatible with the normal reactions of hydration of the components of the cements , as for example organic materials like plant leaves, wood , ….

These normally is the most rough step of this technology and needs a complete characterization of the matrix to be able to choose the proper cements and process parameters.

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2º- Study of the matrix.

As a complement of the data caracterización of Efice Firm and Mayasa of the two industrail wastes , we studied the particle size distribution of these materials and its physical behaviour to treat them :

	Masa Desmercurizante	Barro de salmuera
Tamiz mm.	% pasa	% pasa
8	100	100
6	98,2	100
5	93,7	100
4	14,8	100
3	4,5	100
0,5	2,3	100
0,25	1,1	99,2
0,16	0,6	97,6
0,063	0,2	92,6

	% H2O
Masa Desmercurizante	9,7
Barros de Salmuera	34,4

Both materials don’t present chemical problems for the hydration of the cements, but the “Masa desmercurizante” presents a monogranular particle size distribution and the “barro de salmuera “ has very small particles , with high surface , high moisture that makes it a very sticky material , difficult to handle.

3º. Select the appropiate cements , admitures and complementary materials.

In this technology with the information of the preceding steps it is chosen the proper cements , the admixtures and complementary materials to treat the contaminants and the matrix .

Microcements are cements with very fine size of particles and there are some different categories, for example :

- -TP32 , that all the particles are below 32 microns, Surface : 7000 cm2/g
- - TP12 That all the particles are below 12 microns Surface : 14.000 cm2 /g
- - TP6 that all the perticles are below 6 micróns Surface : 21.000 cm2/g

These microcements mixed with water and superplastifiers ,as polycarboxilates , let get colloidal suspensions with very high penetration in voids, cracks and internal porosity in the material to treat.

Sulfur microcements stabilize and solidified the contaminated components , in this case , mercury components , in coprecipitation with the cement hydration products.

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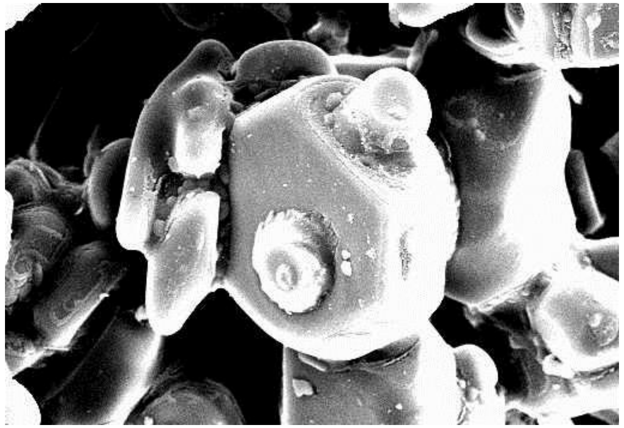
3º. Select the appropiate cements , admitures and complementary materials.

Cements are mainly calcium silicates with other phases (C3A , C4AF ,…) and sulfur components ,as (Na, K ,Ca)SO_4 , and with a proper operation of the sinterization of the clinker, with sulfides components (Na,K)S.



The sulfur components in the clinker are sticking the calcium silicates ,and when the clinker is grinded in small particles , silicates ,sulfides and sulfates keep on together.
In the microcements because its large content of particles below one micron, this particles go to the smaller porous of the material to treat. In this way we get a high surface of reaction between sulfur microcements and the mercury contaminated components .

To treat mercury wastes with metalic mercury an addition of *sulfur* is added to the microcement.

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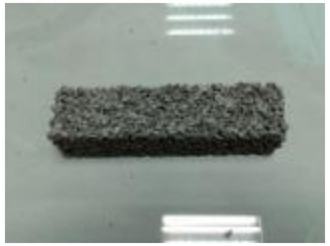
4º. Select the properties of the final material and look for the optimum formulation

In the industrial waste of the material “ Masa Desmercurizante” , as we have said it has a mongranulometric particle size distribution .
Mixing it with a normal ,even high , content of cement , the result is a “porous concrete (pervious concrete)”,



“Masa desmercurizante”tratada

Pervious concrete

This material doesn't meet the requirements of durability needed . It will need a complementary material like a sand with a granulometric range from 0 to 3 mm.

4º. Select the properties of the final material and look for the optimum formulation

On the contrary , the industrial waste " Barros de Salmuera" , it`s very fine , with high surface , high moisture , and because of that very sticky. To get proper durability values ,it is necessary a complementary material like a sand with particle size distribution from 0 to 3mm ,and better other aggregate from 3 to 10 mm , what part of it could be the industrial waste "Masa desmercurizante ".

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"Barro de salmuera" treated

In both cases , not to use complementary materials leads to a expensive solution with high amount of microcement.

4º. Select the properties of the final material and formulation

				Pasa %									% kg/m3
TAMIZ mm		12,50	10,00	8,00	4,00	2,00	1,000	0,500	0,250	0,125	0,063	% Hg	
Microcemento		100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	0,00	300
Barro de salmuera		100,00	100,00	100,00	100,00	100,00	100,00	100,00	99,20	97,30	92,60	0,21	260
ARENA 0-4		100,00	100,00	100,00	99,69	83,86	56,21	37,79	24,52	15,87	10,92	0,0	791
Masa desmercurizante		100,00	100,00	100,00	14,80	4,00	3,00	2,30	1,10	0,80	0,20	6,5	0
ARIDO 4-12		99,05	79,45	41,12	2,20	1,58	1,36	1,30	1,24	1,18	1,05	0,0	945
													0
Curva teórica		100,0	90,9	82,8	62,6	48,4	38,3	31,2	26,2	22,6	20,1		
Curva Real		99,6	91,2	74,8	58,1	52,2	42,2	35,6	30,7	27,4	25,0	**0,02**	1025

$$\sum (x_{curva teórica} - x_{curva.real})^2 = 202$$

				Pasa %									% kg/m3
TAMIZ mm		12,50	10,00	8,00	4,00	2,00	1,000	0,500	0,250	0,125	0,063	% Hg	
Microcemento		100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	0,00	300
Barro de salmuera		100,00	100,00	100,00	100,00	100,00	100,00	100,00	99,20	97,30	92,60	0,21	552
ARENA 0-4		100,00	100,00	100,00	99,69	83,86	56,21	37,79	24,52	15,87	10,92	0,0	386
Masa desmercurizante		100,00	100,00	100,00	14,80	4,00	3,00	2,30	1,10	0,80	0,20	6,5	0
ARIDO 4-12		99,05	79,45	41,12	2,20	1,58	1,36	1,30	1,24	1,18	1,05	0,0	1.057
													0
Curva teórica		100,0	90,9	82,8	62,6	48,4	38,3	31,2	26,2	22,6	20,1		
Curva Real		99,5	90,2	71,8	53,2	50,1	45,2	41,9	39,4	37,4	35,3	**0,05**	1025

$$\sum (x_{curva teórica} - x_{curva.real})^2 = 999$$

4º. Select the properties of the final material and formulation

TAMIZ mm		12,50	10,00	8,00	4,00	2,00	1,000	0,500	0,250	0,125	0,063	% Hg	
Microcemento		100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	0,00	300
Barro de salmuera		100,00	100,00	100,00	100,00	100,00	100,00	100,00	99,20	97,30	92,60	0,21	173
ARENA 0-4		100,00	100,00	100,00	99,69	83,86	56,21	37,79	24,52	15,87	10,92	0,0	731
Masa desmercurizante		100,00	100,00	100,00	14,80	4,00	3,00	2,30	1,10	0,80	0,20	6,5	843
ARIDO 4-12		99,05	79,45	41,12	2,20	1,58	1,36	1,30	1,24	1,18	1,05	0,0	249
													0
Curva teórica		100,0	90,9	82,8	62,6	48,4	38,3	31,2	26,2	22,6	20,1		
Curva Real		99,9	97,7	93,4	56,4	47,0	37,4	31,1	26,2	23,0	20,8	**2,50**	1025

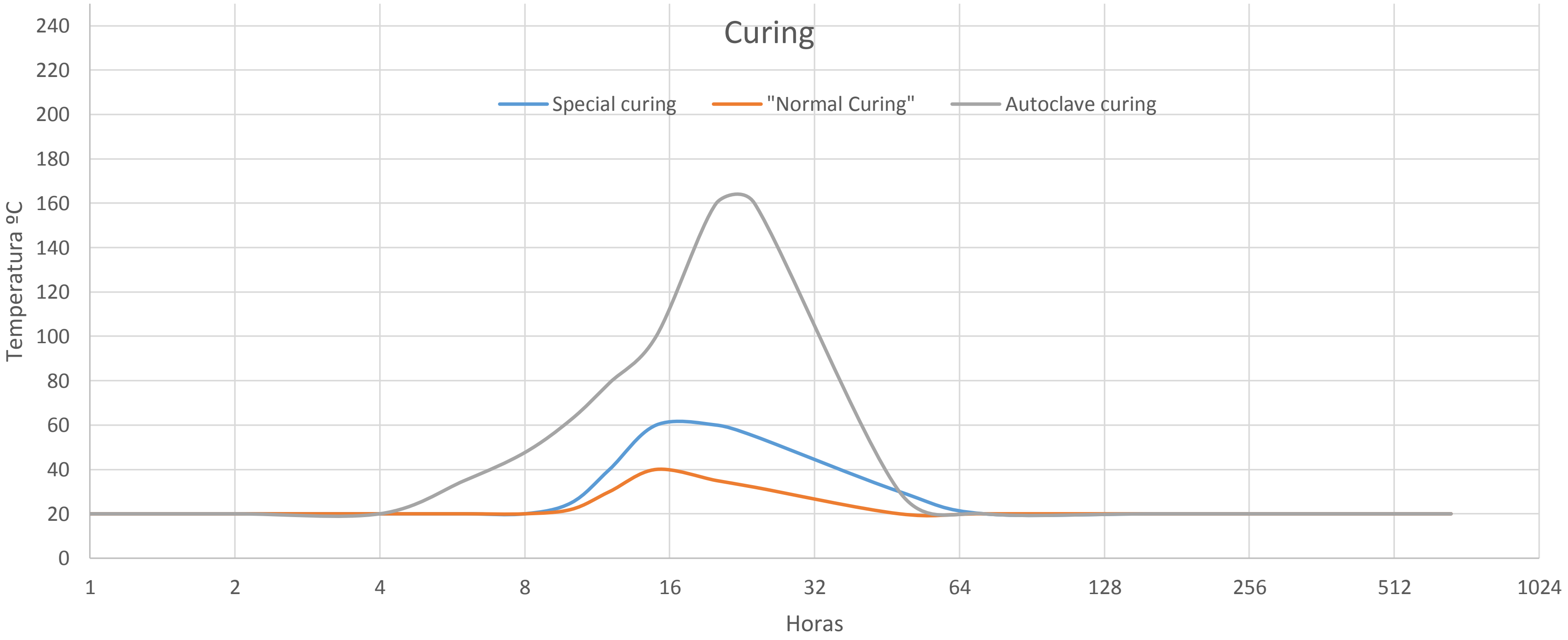
$$\sum \left(x_{curvateórica} - x_{curva.real}\right)^2 = 213$$

5º- Select the process of mixing and curing.

The process of mixing the industrial wastes , the complementary materials , the microcement water and admixtures , has to be in a determinate order , specially with materials like the “Barros de Salmuera “ .
The order of mixing should be, first the sand , second the “barros de salmuera “ , third the course aggregate and finally the colloidal suspension of water and microcement and admixtures.
The curing is main important step to get the proper stabilization of the contaminants components.
Cements , and specially microcements have an important heat of hydration , that lead to high temperatures in its mortars and concretes . That helps the chemical reactions of stabilization. When mixing about 300 kg/m3 , without compaction , just mixing the materials , that we call “Normal Curing” the temperature gets about 40 ºC . But when the material treated goes to a mold with compaction and its size is over 1 m^3 , that we call “ Special Curing”, the temperature rises more than 60 º C . With this “Special Curing” , it is possible increase the maximum temperature, by increasing the dosage of microcements or the size of the mold or adding an external source of heat . And with the appropriate installations, it is possible to reach temperatures over 250 ° C by heat treatments.
Also it’s possible to control the temperature/time function. .

As we can see the cement matrix with this technology becomes to a chemycal reactor.

5º- Select the process of mixing and curing.



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6º- Chemical and Physical Tests in the Lab.

With all the information of the preceding steps , some samples of “ Masa Desmercurizante” y los “Barros de Salmuera” were treated with the following results.

Ensayo	A15	A16	X1	X2	X3	B15	B16	B17	C11	C12	C13
Barro de Salmuera	400		400	400	400	400			260	552	173
Masa Desmercurizante		400	0				400	400	0	0	843
Microcemento TP12	60	60	120	200	200	240	240	400	300	300	300
Arena 0/4		0	0	0	0	0	0	0	791	386	731
Arido 4/12	0	0	0	0	0	0	0	0	945	1057	249
Agua total	137,6	38,8	137,6	137,6	137,6	137,6	88,8	138,8	158	205	156
Aditivo Superplatificante	6	6	24	10	6	24	14	40	18	18	18
Método de mezclado	B	B	B	B	B	B	B	B	C	C	C
Densidad obtenida despés de proceso de maduración	1,23	1,03	1,55	1,68	1,62	1,71	1,54	1,68	2,31	2,29	2,33
Relación agua/cemento	2,29	0,65	1,15	0,69	0,69	0,57	0,37	0,35	0,53	0,68	0,52
% Hg	0,14	5,16	0,12	0,11	0,11	0,10	3,51	2,66	0,02	0,05	2,24
Resistencia a compresión en Mpa UNE EN 1015-11 2000	3,40	2,50	27,20	37,80	32,50	46,70	38,10	47,30	34,10	29,30	47.8
mg/kg Ensayo de Lixiviación UNE EN 12457-4 2003	0,048	0,093	0,009	0,004	0,005	0,004	0,002	0,0007	0,002	0,002	0,007
Peso teórico de la muestra	597,6	498,8	657,6	737,6	737,6	777,6	728,8	938,8	2454	2500	2452
Volumen teórico de la muestra	323,7	261,7	343,7	370,3	370,3	383,7	371,7	475,1	1033,6	1089,2	1132,4
Densidad teórica de la muestra	1,8	1,9	1,9	2,0	2,0	2,0	2,0	2,0	2,4	2,3	2,2
Incremento de volumen después del tratamiento teórico	1,1	1,1	1,2	1,2	1,2	1,3	1,4	1,7	5,0	2,6	1,8
Incremento de volumen real después del tratamiento	1,6	2,0	1,4	1,4	1,5	1,5	2,0	2,3	5,4	2,6	1,6

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7º- Field Trial and Industrial Project.

An initial field trial is very important to get the industrial data for the project of decontamination that it should get all the facilities to be a safe , clean and efficient process.

- 1º- Feeding of the materials to a Mobile Concrete Plant.

2º- Mixing the materials in the mixer of the Plant

All the steps with the necesaries filters and vapour collectors.

3º- Mold pouring and curing :

4º- Storing