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COMPARISON OF THE STABILIZATION/SOLIDIFICATION (S/S) OF THREE GALVANIC WASTES USING CEMENT, CEMENT WITH SOLUBLE SILICATES OR MAGNESIUM PHOSPHATE CEMENTS

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ABSTRACT
The galvanic processes used for coating metallic or plastic surfaces generate wastes that should be properly treated before their disposal in a landfill. Stabilization /Solidification (S/S) converts them to solids and reduces the release of heavy metals. In this study, three real wastes (an exhausted electroless nickel plating bath, an exhausted chromium electroplating bath and a zinc plating sludge) were stabilized using different reagents: Portland cement type I, Portland cement mixed with soluble silicates and magnesium phosphate cements prepared with MgO extrapure or hard burned magnesia of about 70 % purity and phosphates like Na_3PO_4, Na_2HPO_4 *or* KH_2PO_4.
In order to analyze the retention of the heavy metals by the matrix the samples were subjected to the leaching test number 2 of the Spanish Order 13/10/89 (similar to the Toxicity Characteristic Leaching Procedure of the U.S. EPA). Heavy metal concentration of the leachate was determined using ICP-MS.
It was found that magnesium phosphate cements obtained by mixing hard burned magnesia with the different phosphates are appropriate for the Stabilization/Solidification (S/S) of the wastes containing nickel and zinc. The waste containing chromium showed in all cases a Cr(VI) concentration above the limit defined by the U.S.EPA for the disposal of a waste.
Keywords: galvanic wastes, Stabilization / Solidification (S/S), leaching test

1. INTRODUCTION
The galvanic processes like electrolytic plating or electroless plating generate toxic wastes containing high concentration of heavy metals. Such wastes should be properly managed in order to minimize their environmental impact. A usual treatment for aqueous wastes containing heavy metals before landfilling is Stabilization/Solidification (S/S). It consists of mixing the waste with one or more reagents so that the release of metals is reduced and the waste turns into a solid monolith which can be easily handled [1]. Several reagents are effective for the Stabilization/Solidification (S/S) of wastes containing heavy metals: Portland cement, Portland cement with soluble silicates, lime with fly ashes, soluble phosphates, etc. [2].
In this study, three real wastes provided by a galvanic industry were employed: an exhausted nickel electroless plating bath (R1), an exhausted chromium electrolytic plating bath (R2) and a zinc plating sludge (R3). Each waste was mixed with several reagents in order to compare their performance: Portland cement, Portland cement with soluble silicates and different magnesium phosphate cements.

2. MATERIALS AND METHODS

The reagents used were: Portland cement type I, sodium silicate (Na_2SiO_3) pure in neutral solution from Scharlau, magnesia (MgO) extra pure of Scharlau, hard burned magnesia (MgO) of 70 % purity from Magnesitas Navarras S.A., potassium dihydrogen phosphate (KH_2PO_4) extra pure of Scharlau, sodium hydrogen phosphate ($Na_2HPO_4 \cdot 2H_2O$) extra pure of Scharlau and sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) extra pure of Panreac.

The pastes were prepared by mixing the reagents and afterwards adding the wastes R1, R2 and R3. The mix was stirred for 30 min and left for curing for 3 weeks.

A leaching test according to test number 2 of Spanish Order 13/10/89 [3] was performed to all the samples (10 g), with a liquid-solid (L/S) ratio of 20 ml g^{-1} using acetic acid until pH 4. The particle size was < 4 mm. The leaching test is similar to TCLP (Toxicity Characteristic Leaching Procedure) of the US EPA [4] excepting the particle size (< 9.5 mm in TCLP).

The leachate was analyzed by means of ICP-MS (inductively coupled plasma with mass spectrometer) in order to determine the heavy metal concentration as well as the magnesium and total phosphorous concentration.

In order to compare the retention of metals by the different matrices a retention factor R_f *(%)* was defined:

$$R_f = \frac{C_i - C_f}{C_i} \cdot 100 \qquad (1)$$

Where
C_i is the initial quantity of a component at the samples (mg)
C_f is the final quantity of the component at the leachate (mg)

3. RESULTS AND DISCUSSION

3.1. Nickel waste (R1)

The results for R1 are presented at Table 1.

Table 1. Stabilization/Solidification (S/S) of waste R1. Ni, Mg and total phosphorous concentration at the leachate

REAGENTS	% (in weight)	W/S	[Ni]initial (g dm^{-3})	[Ni]leachate (mg kg^{-1})	R_f (Ni)	[Mg]leachate (mg kg^{-1})	[P]leachate (mg kg^{-1})
KH_2PO_4 / MgO extra pure	50/50	2.50	5.4	1154.6	70.07	178026	16441
Na_2HPO_4 / MgO extra pure	50/50	2.33	5.4	864.2	77.14	13418	15689
Na_3PO_4 / MgO extra pure	50/50	1.67	5.4	614.2	81.80	11315	13449
KH_2PO_4 / MgO hard burned	50/50	0.42	5.4	71.7	95.49	3501	8457
Na_2HPO_4 / MgO hard burned	50/50	0.42	5.4	112.7	92.90	116	12129
Na_3PO_4 / MgO hard burned	50/50	0.42	5.4	123.4	92.23	421	7734
Portland cement	100	0.43	5.4	1344.8	16.99	-	-
Portland cement/silicate	85/15	0.43	5.4	987.3	39.06	-	-

At present there are no defined limits for the leachate concentration of Ni according to leaching test TCLP. At Catalonia the maximum admissible leachable content of Ni (leaching test 38414-S4 [6]) is 2 mg dm^{-3} (or 20 mg kg^{-1} for a liquid-to-solid (L/S) ratio of 10 cm^3 g^{-1}) for the disposal of a waste at a class III landfill (special wastes) [7]. Although the results are above the limit in all cases, magnesium phosphate cements prepared with hard burned magnesia show better results than the other reagents (retention factor above 92 %). When using MgO extrapure the retention factor is lower. Both Portland cement and Portland cement with soluble silicates show poor retention factors for Ni.

3.2. Chromium waste (R2)

The results for R2 are shown at Table 2.

Table 2. Stabilization/Solidification (S/S) of waste R2. Total Cr, Mg and total phosphorous concentration at the leachate

REAGENTS	% (in weight)	W/S	[Total Cr]initial (g dm^{-3})	[Total Cr]leachate (mg kg^{-1})	R_f (Cr)	[Mg]leachate (mg kg^{-1})	[P]leachate (mg kg^{-1})
KH_2PO_4 / MgO extra pure	50/50	2.67	11.3	10395.1	0	10689	39
Na_2HPO_4 / MgO extra pure	50/50	1.83	11.3	8731.9	0	2658	71
Na_3PO_4 / MgO extra pure	50/50	1.67	11.3	6486.0	8.16	3150	36
KH_2PO_4 / MgO hard burned	50/50	0.42	11.3	1915.0	42.38	2159	1841
Na_2HPO_4 / MgO hard burned	50/50	0.42	11.3	2061.6	37.97	640	3795
Na_3PO_4 / MgO hard burned	50/50	0.42	11.3	2194.3	33.98	121	102
Portland cement	100	0.43	11.3	1307.3	61.44	-	-
Portland cement/silicate	85/15	0.43	11.3	2037.5	39.90	-	-

Although the best results are provided by Portland cement, in all cases the retention factor for chromium is low and the total Cr concentration is above the limits established by the US EPA for the landfilling of wastes (5 mg dm^{-3} or 100 mg kg^{-1} for a liquid-to-solid (L/S) ratio of 20 cm^{3} g^{-1}) (see also Figure 1). This is probably due to the fact that the chromium in waste R2 is predominantly as hexavalent chromium. Anionic species like CrO_4^{2-} are not expected to be chemically stabilized by the matrices because they do not allow the formation of relatively insoluble compounds like hydroxides or phosphates. Therefore it is usually recommended a previous treatment in order to reduce most hexavalent chromium to trivalent chromium [5].

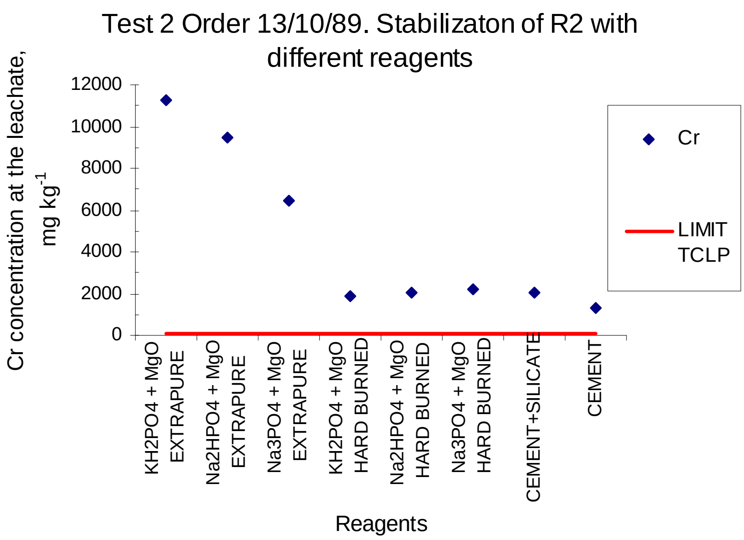

Figure 1. Stabilization/ Solidification of waste R2. Total chromium concentration at the leachate (mg kg^{-1}) and TCLP limit (mg kg^{-1}).

3.3. Zinc waste (R3)

The results for R3 are presented at Table 3.

Table 3. Stabilization/Solidification (S/S) of waste R3. Zn, Mg and total phosphorous concentration at the leachate

REAGENTS	% (in weight)	Waste/water (g cm^{-3})	W/S	[Zn]initial (g kg^{-1})	[Zn]leachate (mg kg^{-1})	R_f(Zn)	[Mg]leachate (mg kg^{-1})	[P]leachate (mg kg^{-1})
KH_2PO_4 / MgO extra pure	50/50	0.28	2.50	278.8	15.6	99.96	8962	18
Na_2HPO_4 / MgO extra pure	50/50	0.5	1.50	278.8	19.7	99.97	5828	46
Na_3PO_4 / MgO extra pure	50/50	0.4	1.83	278.8	5.8	99.99	3523	72
KH_2PO_4 / MgO hard burned	50/50	2.0	0.42	278.8	14.2	99.98	1390	1093
Na_2HPO_4 / MgO hard burned	50/50	0.8	0.42	278.8	10.4	99.98	7319	659
Na_3PO_4 / MgO hard burned	50/50	0.8	0.42	278.8	2.9	99.99	211	298
Portland cement	100	0.5	0.43	278.8	627.4	98.49	-	-
Portland cement/silicate	85/15	0.5	0.43	278.8	306.9	99.20	-	-

There are no limits for the leachate concentration of Zn according to leaching test TCLP. At Catalonia the maximum admissible leachable content of Zn is 10 mg dm^{-3} (or 100 mg kg^{-1}) according to test DIN 38414-S4 for a landfill class III (special wastes). The Zn concentration at the leachate is below the limit for all magnesium phosphate cements with very high retention factors (above 99.96 %). Portland cement and Portland cement show a Zn concentration at the leachate above the limit.

4. CONCLUSIONS

Magnesium phosphate cements prepared with hard burned magnesia are appropriate materials for the Stabilization/Solidification (S/S) of wastes from electroplating and electroless plating processes containing high quantities of heavy metals because of the high retention of divalent cations like Ni^{2+} or Zn^{2+}.

If the waste contains hexavalent chromium the retention is low for all the matrices studied and it is therefore recommended a previous reduction treatment before Stabilization/Solidification (S/S).

5. ACKNOWLEDGEMENTS

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