Use of magnesia cement in industrial waste cementation

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ABSTRACT

The reaction of magnesium oxide (MgO) with solutions of magnesium salts to form strong bonding phases, e.g. the reaction of MgO with $MgCl_2$ results in the formation of a mixture of magnesium oxychloride (MOC) phases, known as Sorel cement, is widely used in industrial flooring, grinding stones and insulating panels applications. An alternative use of this type of cements in stabilisation of industrial wastes is studied herein. In accordance to the results sorel cement was found to be suitable for heavy metal stabilisation.

1. INTRODUCTION

The removal or immobilization of toxic metals from contaminated soils and wastewater is one of the most important issues of environmental remediation. A well-established and highly diversified waste management technique is stabilisation/ solidification (SS). Stabilisation refers to those techniques that reduce the hazardous behaviour of a waste by means of chemical reactions and solidification refers to techniques that generate a monolithic solid of high structrual integrity [1]. A series of cementicious systems have been used for SS of industrial waste which include portland cement, calcium aluminate cements, calcium sulfoaluminate cements, geopolymers and mangesia cements [2].

Magnesia cement (also known as Sorel cement) is a non-hydraulic cement first produced by Stanislas Sorel in 1867 [3]. The bonding phase is created using a mixture of magnesium oxide and magnesium chloride solution to form the desired magnesium oxychloride phase (MOC), according to the reaction:

$$5MgO+MgCl_2+13H_2O \rightarrow 2Mg_3(OH)_5Cl.4H_2O \quad (1)$$
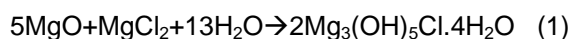
Sorel cement has very good bonding behaviour and decreases significantly the leaching of heavy metals in the environment, while the contained MgO acts as a buffering agent within a pH range of 9–10.5. In this optimum pH heavy metals solubility is minimised and redissolution, that occurs in high pH values using lime or sodium hydroxide, is thus avoided.
SS of wastes using sorel cement system have been used succesfully for sewage sludge [4] and incinerator dust [5] treatment. Furthermore, the influence of certain additives in the sorel system that enhance its water resistance, hence leaching behaviour, have also been studied [6]. In the present article the SS of Electric Arc Furnace Dust (EAFD) and slag from secondary lead production (Pb-RFD) via a sorel cement binding system are studied. Comparative formulations using phosphate ions as additives for water resistance are also investigated.

2. MATERIALS AND METHODS

The two solid wastes used in the present study are depicted in Table 1. The MgO used was a Grecian Magnesite S.A. microcrystalline caustic calcined magnesia (grade 83 CG) of 83,41% nominal purity, specific surface area of 32 m^2/g, milled below 75 μm.

Table 1. Major metal constituents of the two wastes (X-RF)

Element	EAFD[1] (%, dry)	Pb-RF[2] (%, dry)
Mg	3,82	3,00
Al	0,99	0,44
Si	1,94	1,89
Ca	6,33	0,60
Cr	0,18	0,006
Mn	1,80	0,47
Fe	22,41	33,29
Cu	0,24	0,24
Zn	29,49	0,53
Pb	2,63	3,38

[1] Sample supplied by a Greek steel producer
[2] Sample supplied by a Greek lead recycling plant

X-RD analysis of the wastes reveals the presence of the following phases: for the EAFD,

zinc-iron spinel, zinc oxide and sodium chloride, while for the Pb-RF, sodium sulphate, magnetite, hematite, lead sulphide and lead oxides. The EAFD was also found to contain 2,6% free lime.

The magnesium chloride used was a pure industrial grade of $MgCl_2 \cdot 6H_2O$ containing 47% $MgCl_2$.

The MgO was mixed with the waste on various ratios (5, 10, 15, 20 and 25 % w MgO / w dust) and the $MgCl_2$ was added on a stoichiometric ratio following reaction (1). Formulations with 30-50% excess MgO were also prepared. Distilled water was added according to the absorption capacity of the solid mixture and the shaping requirements (pellets, pressed plates and monoliths). H_3PO_4 or KH_2PO_4 were added in several formulations at 1,5 and 5% (MgO basis), respectively, during the mixing stage. Formulations were left to age for 15 days and then sieved or crushed to -10 mm. Leaching experiments were conducted with d.H_2O at an L/S of 10 L/Kg following EN 12457 as specified by 2003/33/EC. Leachates were analyzed by AAS and measured for pH, TDS, DOC, Redox and electrical conductivity. Only the parameters exceeding the non-hazardous limits for the waste-only leaching tests were followed for the stabilized formulations.

3. RESULTS AND DISCUSSION

Several formulations were successful in getting both wastes under the limits for non-hazardous waste. For both wastes, no more than 10-15 % MgO on waste basis was required, while higher MgO addition ratios further reduced the parameter values. Tables 2 and 3 depict the leachate analysis of characteristically stabilized EAFD and Pb-RF formulations at 15 % MgO.

Table 2. Characteristic EAFD stabilization results

Parameter (mg/Kg dry sample)	EAFD only	+ 15 % MgO	Non-Hazardous limits
Shaping	Pellets	Pellets	-
Other Additives	-	No	-
$MgCl_2$	-	Stochiom.	-
Hg	1,5	n.d.	0,01-0,2
Pb	650	2,65	0,5-10
Se	1,2	0,3	0,1-0,5
$SO_4^=$	21.231	6.226	1.000-20.000
Cl-	34.050	49.114	800-15.000
pH	12,3	9,83	-

Chloride anions are an exception. These are often ignored in relevant studies which usually focus on the results of the stabilization of heavy metals only. In the present study, the chlorides are increased in all formulations due to the presence of $MgCl_2$ that has not reacted to form the cement. This increase can be avoided by carefully adjusting the MgO/$MgCl_2$ ratio (i.e. having MgO in excess) and diluting the waste with an inert material when necessary. Note that no formulation was able to get the wastes below the inert waste limits while the addition of either H_3PO_4 or KH_2PO_4 did not improve their stabilization.

Table 3. Characteristic Pb-RF stabilization results

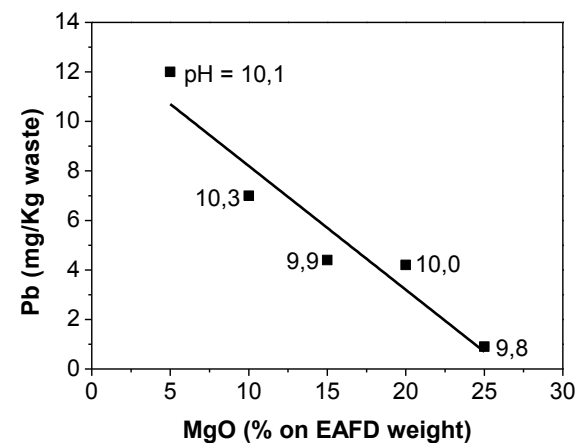| Parameter (mg/Kg dry sample)	Pb-RF only	+ 15 % MgO	Non-Hazardous limits
shaping	powder	monolith	-
Other Additives	-	H_3PO_4	-
$MgCl_2$	-	Stochiom.	-
As	4,5	n.d.	0,5-2
Cd	2,2	n.d.	0,04-6
Hg	1,5	0,02	0,01-0,2
Pb	11	n.d.	0,5-10
Sb	12	0,6	0,06-0,7
Se	4,3	n.d.	0,1-0,5
$SO_4^=$	17.980	16.366	1.000-20.000
Cl-	4.020	27.886	800-15.000
pH	11.2	10.48	-

Figure 1. Effect of % MgO on the leachate Pb concentration. See Table 2 for EAFD only values.

Figure 1 is an example of the effect of MgO addition rate on leachate metal concentration. (lead in stabilized EAFD, shaped in pellets, addition of H_3PO_4, stoichiometric addition of $MgCl_2$). The effect is roughly linear. Even 5% MgO addition results in a dramatic reduction of Pb in the leachate while 10% is enough to go below the 10 ppm non-hazardous limit. This effect can be partly attributed to the pH buffering activity of Sorel and partly to its encapsulative properties. Note that the pH

buffers around 10, below the EAFD-only pH of 12,3 (partly attributed to its free lime content) and in the range where lead (and most heavy metals) reach their lowest solubility. Obviously, addition of MgO only (which is alkaline in nature) does not lower the leachate pH. A possible explanation of the behaviour observed with the current $MgO/MgCl_2$ system is the following reaction,

$$CaO(EAFD\ free\ lime) + MgCl_2 + H_2O \rightarrow$$
$$Mg(OH)_2\downarrow + CaCl_2 \qquad\qquad (2)$$
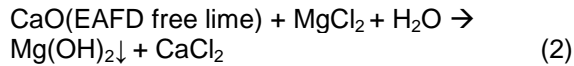
well-known to producers of synthetic MgO from sea-water or brines[7]. The newly formed magnesium hydroxide will know contribute to pH buffering along with the Sorel cement and any excess MgO in the formulation. The above reaction is also a possible explanation of the fact that addition of H_3PO_4 did not enhance stabilization performance further, as seen elsewhere [8].

3. CONCLUSIONS

Greek microcrystalline CCM in Sorel cement systems is very promising for the stabilization of EAF and Pb-RF dusts. Use of MgO in the order of 10-15 % on dust weight basis added in certain ratios along with $MgCl_2$, was found enough to stabilize the wastes below the non-hazardous limits. Cement system optimization can improve performance further. To this end, chloride-free systems, such as magnesium phosphate cement will be the object of future study.

REFERENCES

[1] Coz A, Andres A, Soriano S, Irabien A, 2004. Environmental behaviour of stabilised foundry sludge. *J.Hazard.Mater.*, B109: 95-104.
[2] Sharp JH, Hill J, Milestone NB, Miller EW, 2003. Cementitious systems for encapsulation of intermediate level waste. In: *Proc. 9*th *Int. Conf. on Radioactive Waste Management and Environmental Remediation,* ICEM, Oxford, England, pp.1-10.
[3] United States Patent No. 53092, 1866.
[4] Jianli M, Youcai Z, Jinmei W, Li W, 2010. Effect of magnesium oxychloride cement on stabilization/solidification of sewage sludge. *Constr. Build. Mater.*, 24(1): 79-83.
[5] Mačáková S, Šiška F, Pliešovská N, Hepworth MT, 1996. Solidification of fly ash from municipal solid waste incinerator by the use of sorel cement. *Acta Montan.Slov.*, 1: 35-42.
[6] Deng D, 2003. The mechanism for soluble phosphates to improve the water resistance of magnesium oxychloride cement. *Cem. Concr. Res.,* 33: 1311-1317.
[7] Shand, MA, 2006. The Chemistry and Technology of Magnesia. Wiley, N.J.
[8] Mitrakas, MG, Sikalidis CA, Karamanli TP, 2007. Immobilization of EAFD heavy metals using acidic materials. *J. Envi. Sci. Heal.* Pt A., 42: 535-541.