

Experimental study of the waste binder anhydrite in the solidification/stabilization process of heavy metal sludges

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Abstract

An experimental study of the use of an industrial byproduct, anhydrite (CaSO_4), as inorganic binder in the solidification/stabilization (S/S) process of heavy metal sludges has been performed. The influence of the variables: binder:waste ratio, anhydrite particle size and water amount on the S/S process of a synthetic sludge containing Cd, Cr and Pb has been studied. Leaching of stabilized products using the Toxicity Characterization Leaching Procedure was used to evaluate the behaviour of heavy metals after treatment with anhydrite. Significant reductions of leached metal concentrations were achieved depending on the experimental variables. Therefore, it has been shown the possibility to use anhydrite as binder in S/S processes of wastes containing heavy metals and the influence of the main variables in the S/S process, in order to satisfy landfill disposal regulations. © 1998 Elsevier Science B.V.

Keywords: Anhydrite; Inorganic binder; Solidification/stabilization

1. Introduction

Among the types of hazardous industrial wastes, materials containing heavy metals are an important group due to its high volume and accumulation in the environment. It is well known that heavy metals are of environmental concern. They are hazardous to humans and to other forms of life. This group of wastes presents a great diversity of composition attending to the origin, therefore a study of the behaviour of different types of heavy metal wastes can be recommended.

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A synthetic sludge containing cadmium, chromium and lead has been considered as a reference material, which behaviour can be related to industrial heavy metal sludges. These industrial wastes are very important due to the large generation rate and environmental impact. Among them Steel Foundry Dust (SFD) is the solid or sludge material recovered from filtration units in steel factories [1]. The toxicity of SFD has been reported previously using different leaching test procedures, involving characterization of leachate by chemical analysis and biotoxicity evaluation [2]. From the obtained results SFDs were classified as hazardous wastes, and therefore they require the application of treatment technologies, which must be carefully checked in order to establish the experimental behaviour of the heavy metal leaching.

Solidification/stabilization (S/S) technologies are defined as treatment processes designed not only to improve waste-handling and physical characteristics, but also to decrease surface area across which pollutants can transfer or leach, limit the solubility of contaminant compounds and detoxify the hazardous constituents [3]. S/S technologies are used widely for treating both inorganic and organic waste materials. Unfortunately some of these processes have turned out to be simple adsorption/dilution phenomena. For true S/S process, the binder and the waste must interact chemically to create chemical bonding [4,5]. At present these technologies are presented as acceptable methods for obtaining final products that satisfy the guidelines of landfilling.

The selection of a S/S process in comparison to other possibilities of treatment of wastes or to the recovery, recycling or reuse processes is based on technical and/or economical reasons [6]. In the case of heavy metal wastes, there are, however other more compelling reasons such as the recovery processes themselves which generate wastes that still contain metals often in a more leachable form or recovery processes, which are not available to remove hazardous metals from industrial wastes below the levels of environmental concern [7,8].

The main S/S technologies are patented processes, which consist in the mixing of variable amounts of binder and additive reagents with the specific waste. Most of the processes are included into few generic types, allowing, multiple applications because of the increasing number of wastes to be treated. In some cases a waste can be used in the formulation of the binder [9].

S/S processes differ among themselves basically in the type of treated waste and in the chemicals used in the process. Wastes, which present toxicity by heavy metals are able to be detoxified by many existing S/S processes, but in some cases they cannot be mixed with acidic solutions since they neutralize the low solubility hydroxides, in these processes it is possible to use inorganic or organic binders [10,11].

For many types of hazardous wastes, specially in the case of heavy metals, S/S usually leads to excellent results for long-term immobilization. Conner has described and reviewed some commercial applications [7]. Several patented processes currently use cement-based or pozzolanic cement-based processes to stabilize the contaminant within a solid matrix. The most common processes use portland cement or pozzolans such as fly ash, cement kiln dust, lime or combinations of these materials. Heavy metals are converted to hydroxides and silicates due to the alkaline environment of these mixtures [12]. However, it appears that the scientific basis for the solidification/stabilization of wastes is not well documented. Because each chemical element has a unique

chemistry, its interaction with the binder must, in general, be studied separately. On the other hand, researchers have investigated stabilization using different leaching procedures [13–17] and different types of wastes [18,19]. Recently, stabilization mechanisms have also been discussed [20–23].

Taking into account the great number of methods to immobilize wastes, the most suitable method to be applied will be those that use the most economic inorganic raw materials, fulfilling environmental regulations.

The scope of this paper is the experimental study of the possible use of an industrial byproduct (*anhydrite*) in the stabilization of heavy metals and the influence of the main variables in the heavy metals lixiviation of the final product, according to the Toxicity Characterization Leaching Procedure. The byproduct, anhydrous calcium sulfate (CaSO_4) known as anhydrite, obtained from the hydrofluoric acid (HF) manufacturing process, is a potential binder, that satisfies all the initial requirements to be used in S/S processes. This material has a great affinity with water, it is able to form a hydrate and it can be dried and converted into a consistent material. At the moment this byproduct is being generated in large amounts and disposed in landfills [24], depending on the market.

The hydration mechanism of anhydrite is very similar to the hydration of dehydrated gypsum which has been suggested as binder material in S/S processes, Förstner [25], although the hydration rate is much more slower. Capacity of hardening and setting is produced by the rehydration to di-hydrate. This is the source of its use as an aerial binder. The anhydrite is a source of raw material for formulating several commercial cements, such as oversulphated slag cement of high resistance to sulphates [26].

A characterization study of the byproduct anhydrite, was carried out and its application as inorganic binder was evaluated in S/S processes of laboratory heavy metal sludges. The toxicity evaluation of the final products was based on the leaching test procedure, TCLP (Toxicity Characterization Leaching Procedure), standardized by the U.S. Environmental Protection Agency [27] and chemical analysis of heavy metals in the leachate. In this work the influence of the processing variables (a) binder:waste ratio (b) anhydrite particle size and (c) percentage of water on the leaching behaviour of the final solids has been analysed using a factorial design of experiments, leading to the basis for the design and optimization of the above mentioned S/S process.

2. Materials and methods

2.1. Synthetic waste

A synthetic waste solution was prepared by addition of 0.04 M each of cadmium (as $\text{Cd}(\text{NO}_3)_2$), chromium (as CrCl_3) and lead (as $\text{Pb}(\text{NO}_3)_2$), to distilled water. This resulted in a solution with a pH of 3.0. The solution was treated with lime up to a pH of 9.5 to produce a sludge. The laboratory waste was generated after dewatering this sludge to a total solids amount of 33.0%. The obtained waste was denominated 'dry sludge'. A chemical characterization of the laboratory waste is shown in Table 1.

Table 1
Chemical characterization of the synthetic waste

| TCLP leachate | Chemical characterization (mg/l) | | | |
|------------------|----------------------------------|------------|------------|------------|
| | pH | Pb | Cr | Cd |
| Initial solution | 3.0 ± 0.2 | 5600 ± 100 | 1907 ± 190 | 5783 ± 202 |
| Dry-sludge | 6.11 ± 0.06 | 1678 ± 165 | 853 ± 55 | 5800 ± 96 |

2.2. Waste binder (anhydrite)

Anhydrite (CaSO_4) was obtained from Derivados del Fluor, Onton, Cantabria, as a residual byproduct of the hydrofluoric acid (HF) manufacture, where the hydrofluoric acid is obtained by the reaction between dry fluorspar (CaF_2) and sulfuric acid (H_2SO_4).

2.3. Toxicity evaluation

The characterization of the heavy metals sludge was evaluated using the TCLP (Toxicity Characterization Leaching Procedure). The procedure involves a high liquid:solid (waste) ratio (2 l:100 g), which is stirred at 30 rpm over 18 h. The extraction solution is selected as a function of the alkalinity of the solid waste (Acetic acid or acetic acid/sodium hydroxide) [27]. After completion of the test the leachate was filtered and tested for biotoxicity (EC_{50}) and heavy metals concentration.

Analysis of the metal ions Pb, Cr and Cd in the leachate, was carried out using a Perkin Elmer 1100B Atomic Absorption Spectrometer. The results were compared to the limits defined in the U.S. Environmental Protection Agency regulations [28], i.e. Cr < 5 mg/l, Pb < 5 mg/l, and Cd < 1 mg/l.

The characterization of the byproduct anhydrite was performed in the TCLP leachate by the luminiscence bioassay technique based on the marine bacterium *Photobacterium Phosphoreum* using a Microtox Toxicity Analyzer, M-500 (Microbics, Carlsbad, CA). The standard method is based on the light diminution of bioluminescent bacterial cells when mixed with toxic substances.

2.4. Experimental procedure

Synthetic sludge samples were mixed with anhydrite and water in a CEMEX W-20, X-02-G laboratory scale solid mixer prototype. Subsamples of each mixture were transferred to plastic vessels and cured at room temperature. After different curing times (14, 28 and 56 days), the samples were crushed. The fraction passing a 4.0 mm screen and retained on a 1.0 mm screen was used for leachate determinations by TCLP.

A two level factorial design of experiments was planned in order to study the influence of the following variables or factors; (1) binder:waste ratio, $B:WS$ (g:g); (2) anhydrite average particle size, D_p ; and (3) percentage of water, $\%W = MW / (B + WS + MW)$ ($\text{g/g} \times 100$) on the behaviour of the solidified/stabilized products. These three main factors have been studied as independent variables and four responses or dependent variables have been obtained. Table 2 lists the values of the three factors in the

Table 2
Variables and levels in the factorial design

| Variable | Level | | |
|---|------------------------|-----------------------|------------------------|
| | Minimum ($X_i = -1$) | Central ($X_i = 0$) | Maximum ($X_i = +1$) |
| Binder:waste ratio, $B:WS$ (g:g) | $(B:WS)_m = 2:1$ | $(B:WS)_o = 10:1$ | $(B:WS)_M = 18:1$ |
| Particle size, Dp (mm) | $(Dp)_m = 0.1$ | $(Dp)_o = 0.6$ | $(Dp)_M = 1.1$ |
| Water amount, $\%W$ (g/g $\times 100$) | $(\%W)_m = 12$ | $(\%W)_o = 17$ | $(\%W)_M = 22$ |

experimental design. The central points were selected according to considerations reported in the literature [29,30] and previous works [31,32]. The relation between the values of codified variables (X_i) and real values of the mentioned variables are:

$$X_1 = \frac{B:WS - (B:WS)_o}{[(B:WS)_M - (B:WS)_m]/2}$$

$$X_2 = \frac{Dp - (Dp)_o}{[(Dp)_M - (Dp)_m]/2}$$

$$X_3 = \frac{\%W - (\%W)_o}{[(\%W)_M - (\%W)_m]/2}$$

The maximum (M), minimum (m) and central (o) values of the experimental variables are shown in Table 2

The dependent variables are the concentration of these researched metals usually considered as hazardous: lead, chromium and cadmium. Humidity of final solids was also determined. The influence of the curing time was studied on the S/S process. The evaluation of the lixiviation (TCLP) of the final products after 14, 28 and 56 days was carried out.

3. Results and discussion

The byproduct anhydrite was evaluated according to the Spanish regulations, based on the biotoxicity of the leachate and following the U.S. Environmental Protection Agency regulation, based on the concentration of Pb, Cr and Cd in the leachate. From the obtained results (anhydrite) may be classified as an inert industrial waste, the results of the analysis are reported in Table 3.

The TCLP results of the synthetic waste allow us to estimate the toxicity level taking

Table 3
Characterization of the by-product anhydrite

| TCLP leachate | (mg/l) | | | |
|-------------------------------|----------------------------|-----------------|-----------------|---------------|
| Sample | pH | Pb | Cr | Cd |
| Anhydrite | 5.18 ± 0.10 | 0.85 ± 0.10 | 0.12 ± 0.02 | 0.6 ± 0.1 |
| EC_{50} (mg/l) | | | | |
| $= 11.320 \pm 70$ | | | | |
| Porosity (ϵ) = 69% | Humidity = 2.8% | | | |
| Particle size < 2 mm | Leachate color = colorless | | | |

into account the limits defined in the U.S. Environmental Protection Agency regulation (Cr < 5 mg/l, Pb < 5 mg/l, and Cd < 1 mg/l).

The parameter EC_{50} (effective concentration which decreases 50% of the light normally produced) was compared to the value $EC_{50} = 3000$ mg/l given by the Spanish regulations for toxicity characterization of industrial wastes [33] and the result is reported in Table 3, $EC_{50} = 11,320 \pm 70$ mg/l.

According to the variables and levels shown in Table 2, the results of the S/S process are presented in Table 4, as the percentage of metals retained within the stabilized products obtained from the synthetic waste, corresponding to 14, 28 and 56 days of curing time.

The parameters of the factorial design of experiments are shown in Table 5. It is important to note that the central point of the experimental design does not agree well with the mean value of the linear model, it demonstrates the non-linear influences of the variables, making necessary experimental studies, where at a fixed value of the main variable (*B:WS*, ratio), the influence of the other processing variables could be properly modelled (non-linear models).

The form of the final product is linked to the amount of water in the process. Monolithic blocks have been obtained with sufficient water in the mixture, while the predominant form was granular with less amount of water. The same results were observed for different curing times.

The central point of the factorial design and the average values obtained from the experimental design show the following metal immobilization ability: fraction of fixed lead > fraction of fixed cadmium > fraction of fixed chromium, being lead 30% less mobile than chromium, and 15% less mobile than cadmium in the average value of the experimental results. The same behavior is also appreciated at different curing times.

Although the reduction of the metal concentration in the leachates can be high, 99% of Pb, 93.5% of Cd, and 87.6% of Cr, the leachate concentration of metals do not reach U.S. Environmental Protection Agency regulations (Cr < 5 mg/l, Pb < 5 mg/l, and Cd < 1 mg/l).

After fitting the experimental results of the factorial design to a linear model, coefficients are shown in Table 5, leading to the following linear correlations (Eqs. (1)–(9)).

$$Y_{(\text{Pb}\%, 14 \text{ days})} = 90.0 + 7.2 X_1 + 4.5 X_2 + 0.2 X_3, \quad (1)$$

$$Y_{(\text{Cr}\%, 14 \text{ days})} = 63.3 + 22.8 X_1 + 0.8 X_2 - 1.9 X_3, \quad (2)$$

$$Y_{(\text{Cd}\%, 14 \text{ days})} = 74.9 + 18.0 X_1 + 2.2 X_2 + 0.4 X_3, \quad (3)$$

$$Y_{(\text{Pb}\%, 28 \text{ days})} = 94.6 + 3.5 X_1 + 1.8 X_2 - 0.2 X_3, \quad (4)$$

$$Y_{(\text{Cr}\%, 28 \text{ days})} = 60.7 + 24.8 X_1 - 0.4 X_2 + 2.7 X_3, \quad (5)$$

$$Y_{(\text{Cd}\%, 28 \text{ days})} = 76.1 + 16.8 X_1 + 2.7 X_2 + 0.5 X_3, \quad (6)$$

$$Y_{(\text{Pb}\%, 56 \text{ days})} = 91.0 + 6.9 X_1 + 4.2 X_2 - 0.3 X_3, \quad (7)$$

$$Y_{(\text{Cr}\%, 56 \text{ days})} = 60.6 + 25.1 X_1 - 0.07 X_2 - 0.7 X_3, \quad (8)$$

$$Y_{(\text{Cd}\%, 56 \text{ days})} = 75.7 + 16.8 X_1 + 2.4 X_2 + 0.05 X_3, \quad (9)$$

Table 4
Results of toxicity evaluation (TCLP) for the initial waste and S/S forms

| Sample | B:WS | Dp (mm) | W (%) | Humidity | Reduction | Percentage (%) | |
|-----------------|------|---------|-------|------------|------------|----------------|------------|
| | | | | | Pb | Cr | Cd |
| <i>14 days</i> | | | | | | | |
| M ₁ | 2:1 | 1.1 | 12 | 11.4 | 90.5 | 47.4 | 61.9 |
| M ₂ | 2:1 | 0.1 | 12 | 12.0 | 74.7 | 42.0 | 50.7 |
| M ₃ | 2:1 | 1.1 | 22 | 22.0 | 89.8 | 35.7 | 59.8 |
| M ₄ | 2:1 | 0.1 | 22 | 19.3 | 76.2 | 36.5 | 55.2 |
| M ₅ | 18:1 | 1.1 | 12 | 12.2 | 98.9 | 86.5 | 93.5 |
| M ₆ | 18:1 | 0.1 | 12 | 11.0 | 95.2 | 84.8 | 91.9 |
| M ₇ | 18:1 | 1.1 | 22 | 19.0 | 98.8 | 86.5 | 93.3 |
| M ₈ | 18:1 | 0.1 | 22 | 22.0 | 95.9 | 86.7 | 92.7 |
| M ₀₁ | 10:1 | 0.6 | 17 | 16.1 | 92.2 | 76.8 | 86.6 |
| M ₀₂ | 10:1 | 0.6 | 17 | 15.2 | 92.8 | 76.9 | 87.2 |
| M ₀₃ | 10:1 | 0.6 | 17 | 14.6 | 92.7 | 78.7 | 87.1 |
| M _{0m} | – | – | – | 15.3 ± 0.9 | 92.6 ± 0.3 | 77.5 ± 1.1 | 87 ± 0.3 |
| <i>28 days</i> | | | | | | | |
| M ₁ | 2:1 | 1.1 | 12 | 12.8 | 93.4 | 36.7 | 65.5 |
| M ₂ | 2:1 | 0.1 | 12 | 12.2 | 90.0 | 33.0 | 51.7 |
| M ₃ | 2:1 | 1.1 | 22 | 21.8 | 94.6 | 32.2 | 63.4 |
| M ₄ | 2:1 | 0.1 | 22 | 17.0 | 86.7 | 41.5 | 56.9 |
| M ₅ | 18:1 | 1.1 | 12 | 11.4 | 98.9 | 87.6 | 93.1 |
| M ₆ | 18:1 | 0.1 | 12 | 12.2 | 97.0 | 84.3 | 92.2 |
| M ₇ | 18:1 | 1.1 | 22 | 18.6 | 98.8 | 84.8 | 93.4 |
| M ₈ | 18:1 | 0.1 | 22 | 21.8 | 97.7 | 85.5 | 92.9 |
| M ₀₁ | 10:1 | 0.6 | 17 | 16.0 | 96.5 | 78.5 | 87.7 |
| M ₀₂ | 10:1 | 0.6 | 17 | 15.0 | 96.7 | 79.2 | 87.6 |
| M ₀₃ | 10:1 | 0.6 | 17 | 15.4 | 96.6 | 79.8 | 88.1 |
| M _{0m} | – | – | – | 15.5 ± 0.5 | 96.6 ± 0.1 | 79.2 ± 0.7 | 87.8 ± 0.3 |
| <i>56 days</i> | | | | | | | |
| M ₁ | 2:1 | 1.1 | 12 | 10.1 | 92.2 | 36.5 | 64.0 |
| M ₂ | 2:1 | 0.1 | 12 | 9.8 | 77.0 | 35.7 | 53.0 |
| M ₃ | 2:1 | 1.1 | 22 | 20.3 | 92.3 | 32.5 | 63.0 |
| M ₄ | 2:1 | 0.1 | 22 | 17.2 | 75.0 | 37.4 | 55.9 |
| M ₅ | 18:1 | 1.1 | 12 | 8.5 | 98.4 | 89.0 | 93.3 |
| M ₆ | 18:1 | 0.1 | 12 | 8.6 | 97.6 | 84.0 | 92.4 |
| M ₇ | 18:1 | 1.1 | 22 | 16.0 | 98.2 | 84.2 | 92.2 |
| M ₈ | 18:1 | 0.1 | 22 | 18.6 | 97.5 | 85.7 | 92.0 |
| M ₀₁ | 10:1 | 0.6 | 17 | 12.0 | 97.3 | 78.9 | 89.0 |
| M ₀₂ | 10:1 | 0.6 | 17 | 11.8 | 97.2 | 79.2 | 89.0 |
| M ₀₃ | 10:1 | 0.6 | 17 | 12.2 | 97.5 | 77.5 | 88.8 |
| M _{0m} | – | – | – | 12.0 ± 0.2 | 97.3 ± 0.2 | 78.5 ± 0.9 | 88.9 ± 0.1 |

The pH of the leachates lie in the range between 4.5 and 5.5, close to the pH obtained in the characterization of the raw waste and binder, anhydrite. It has not been found any influence of the curing time in the leachate pH. In the range of the investigated processing variables, the amount of water shows a slight influence on the results of the

Table 5
Parameters of the factorial design of experiments

| Variable | | Humidity (%) | Reduction Pb | Percentage Cr | (%) Cd |
|----------------|-------|--------------|-----------------|------------------|-----------|
| <i>14 days</i> | | | | | |
| \bar{y} | | 16.1 | 90.0 | 63.3 | 74.9 |
| (B:WS) | a_1 | -0.06 | 7.2 | 22.9 | 18.0 |
| (Dp) | a_2 | 0.04 | 4.5 | 0.8 | 2.2 |
| (%W) | a_3 | 4.5 | 0.2 | -1.9 | 0.4 |
| \bar{c} | | 15.0 | 92.6 | 77.5 | 87.0 |
| <i>28 days</i> | | | | | |
| \bar{y} | | 16.0 | 94.6 | 60.7 | 76.1 |
| (B:WS) | a_1 | 0.02 | 3.5 | 24.8 | 16.8 |
| (Dp) | a_2 | 0.2 | 1.8 | -0.4 | 2.7 |
| (%W) | a_3 | 3.8 | -0.2 | 0.3 | 0.5 |
| \bar{c} | | 15.5 | 96.6 | 79.2 | 87.8 |
| <i>56 days</i> | | | | | |
| \bar{y} | | 13.6 | 91.0 | 60.6 | 75.7 |
| (B:WS) | a_1 | 0.7 | 6.9 | 25.1 | 16.8 |
| (Dp) | a_2 | 0.09 | 4.2 | -0.07 | 2.4 |
| (%W) | a_3 | 4.4 | -0.3 | -0.7 | 0.05 |
| \bar{c} | | 12.0 | 97.3 | 78.5 | 88.9 |

\bar{y} : mean value of linear model.

\bar{c} : central point of the experimental design.

a_1 , a_2 and a_3 are the coefficients of the linear fitting.

leaching process of metals, although in previous works on S/S of sludges containing heavy metals with different humidity it was observed a relationship between humidity of the sludge and leaching of metals when wastes are under the influence of weak acids (leaching tests as TCLP, EP, etc.) [34], which could be explained by the non-linear influences in the leaching behaviour.

The binder:waste ratio shows the main influence on the solidification/stabilization process for the three studied metals, as it is shown in the linear correlation of the experimental results. The effect of the B:WS ratio is more clearly visualized in Fig. 1. Instead of the experimental variable, B:WS + B has been represented in order to separate the dilution effect on the waste, this figure can be correlated by a linear expression:

$$(\% \text{ retained metal}) = \alpha + \beta(B:WS + B)$$

where, a mean value of α and β can be fitted for each metal as it is shown in Table 6. This variable, B:WS ratio, has an important influence on the percentage of retained metals: Cr ($a_1 = 22.86$), Cd ($a_1 = 18.0$) and Pb ($a_1 = 7.2$). It is to be remarked that chromium, which shows the lower reduction, is the most sensitive element to the waste:binder ratio.

From the linear fitting of the experimental planning can be observed that in the case of Cd and Pb, bigger particles of anhydrite lead to a lower concentration of metal in the

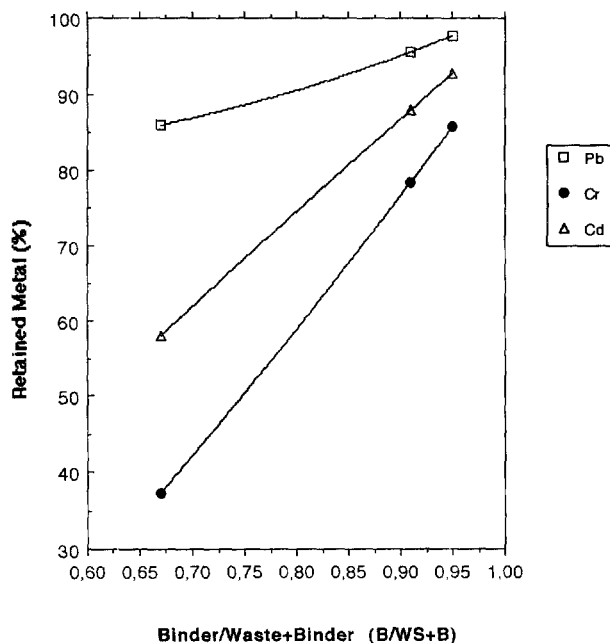


Fig. 1. Retained metals vs binder:waste + binder ratio.

leachate, providing evidence of a higher retention of these metals in the S/S products. In the case of Cr, the influence of this variable is very reduced and it can be neglected. This influence is coupled with the *B:WS* ratio as it is shown in Figs. 2–4, where at low *B:WS* ratios higher retention for Cd and Pb can be found (continuous line) and at high *B:WS* ratios a negligible influence of this variable is found.

From the results of the two level factorial design of experiments a negligible influence of the water amount on the leachate was observed which is in the range of the experimental error of the central point. Fig. 5 shows the negligible influence of this variable. Therefore it is possible to conclude that minimization of the amount of water would be a recommendation for practical purposes, in order to reduce the total amount of waste. Results show that the particle size influences slightly the leaching of metals but does not show any influence in the leachate pH.

Due to the negligible influence of the water amount and the slight influence of the anhydrite particle diameter in the leaching of the heavy metals of the stabilized sludge, in the researched range of variables, the main immobilization capacity is related to the

Table 6

Parameters of the linear fitting of % retained metals vs. *B:WS + B* ratio

| Metal | α | β | r^2 |
|-------|----------|---------|-------|
| Pb | 58.6 | 40.9 | 0.99 |
| Cr | -78.3 | 172.5 | 1.00 |
| Cd | -24.9 | 37.3 | 1.00 |

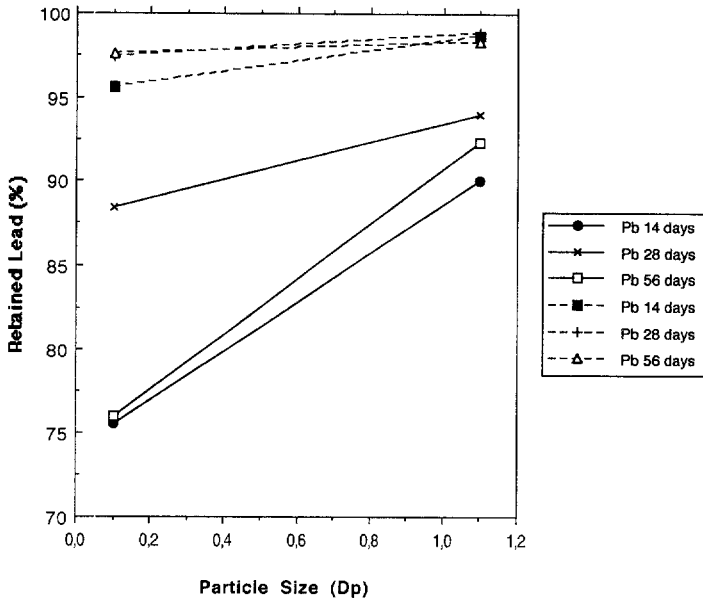


Fig. 2. Retained lead (%) vs particle size in the experimental design; ---, high B:WS ratio; ———, low B:WS ratio.

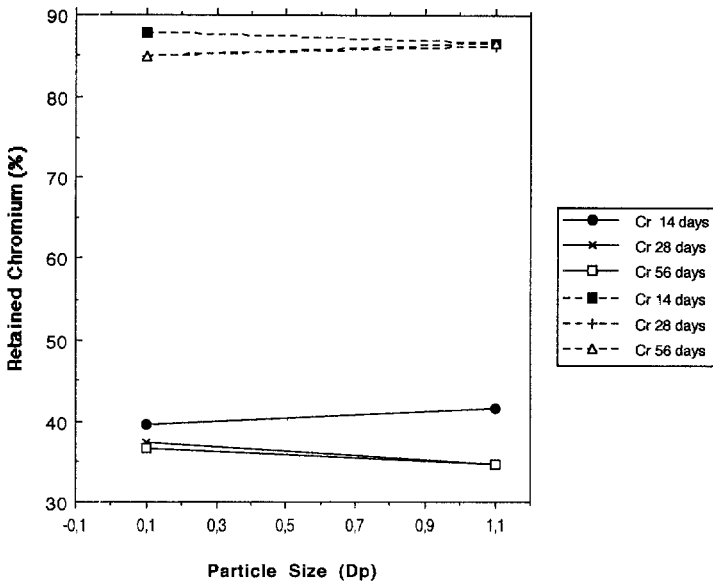


Fig. 3. Retained cadmium (%) vs particle size in the experimental design; ---, high B:WS ratio; ———, low B:WS ratio.

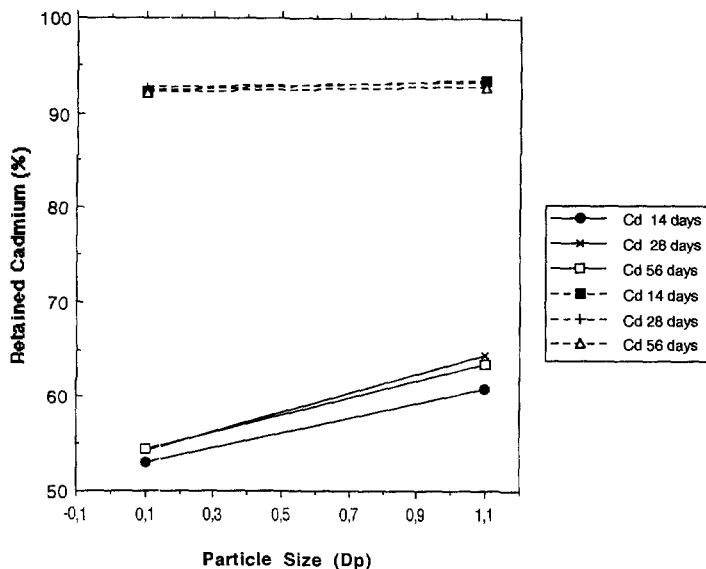


Fig. 4. Retained chromium (%) vs particle size in the experimental design; ---, high B:WS ratio; —, low B:WS ratio.

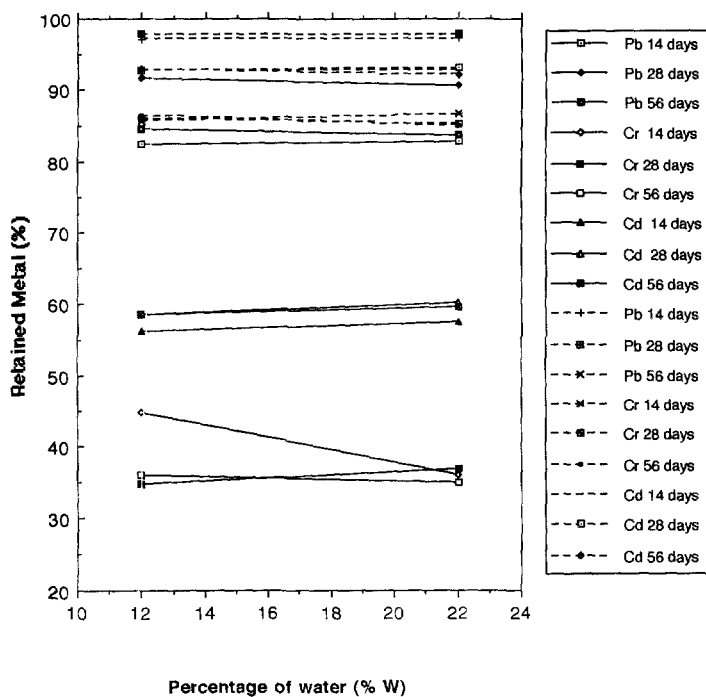


Fig. 5. Retained metals vs percentage of water in the experimental design; ---, high B:WS ratio; —, low B:WS ratio.

B:WS ratio; but an optimization of the anhydrite particle diameter and amount of water should be performed for practical uses, once established the required level of retention for the specific waste at a defined value of the *B:WS* ratio to optimize the S/S process.

For the three metals it can be found a combination of the variables leading to a heavy metal lixiviation near to 90% lower than the synthetic sludge. The optimization of this process is going to be conditioned by the specific type of waste to be treated, but this result show that the mobility of the metal ions can be strongly reduced depending mainly on the binder:waste ratio. Therefore these results show that the solid byproduct 'anhydrite' is useful to retain fractions larger than 90% of the heavy metals usually considered hazardous, concluding its binder suitability to develop Solidification/Stabilization processes for hazardous wastes containing heavy metals in order to achieve the regulations of disposal in landfills.

4. Conclusions

The toxicity of the byproduct, anhydrite, was evaluated according to U.S. Environmental Protection Agency regulations based on the Toxicity Characterization Leaching Procedure, TCLP, for heavy metals concentration, and to Spanish regulations, based on the biotoxicity of the leachate. Taking into account these regulations this waste material can be classified as an inert by-product.

The waste binder, anhydrite, has been used in the Solidification/Stabilization process of a synthetic waste generated in laboratory containing Pb, Cr, and Cd. The study was performed by means of a factorial design of experiments considering as independent variables the binder:waste ratio (2:1–18:1), anhydrite particle size (0.1 mm–1.1 mm) and the percentage of water (12–22%), and as dependent variables, the concentration of the metals Pb, Cd, and Cr in the leachate. The study was carried out for 14, 28 and 56 days of curing time.

It is concluded that significant reductions are achieved in the metal leaching. Lead, cadmium and chromium mobility can be reduced near to 90%, depending on the processing variables: binder:waste ratio, particle diameter of the binder and water amount in the mixture; according to the Toxicity Characterization Leaching Procedure (TCLP). Therefore, it has been experimentally shown the possibility to use anhydrite as binder in S/S processes of hazardous wastes containing heavy metals, in order to satisfy defined regulations of landfill disposal.

Additional optimization of the S/S process should be performed carefully for each type of industrial waste, in order to comply with the requirements of the specific regulations, taking into account that the binder:waste ratio seems to be the main influence in the process, the particle diameter of anhydrite shows a slight influence and the amount of water should be minimized.

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