

REMOVAL OF H₂S BY METAL FERRITES PRODUCED IN THE PURIFICATION OF METAL-BEARING WASTE WATER. STUDY OF THE REACTION MECHANISM

E. BARRADO^{1*}, F. PRIETO³, B. LOZANO¹, F. J. ARENAS¹ and J. MEDINA²

¹ Departamento de Química Analítica; and ² Departamento de Física de la Materia Condensada, Cristalografía y Mineralogía, Universidad de Valladolid, 47005 Valladolid, Spain; ³ Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Hidalgo, Crta. Pachuca-Tulancingo km 4,5, 42076 Pachuca, Hidalgo, Mexico

(* author for correspondence, e-mail: ebarrado@qa.uva.es)

(Received 17 December 1999; accepted 2 October 2000)

Abstract. Waste water polluted with heavy metals can be successfully purified by precipitation of the metals from an alkaline solution containing iron (II), giving rise to a ferrite sludge. The solid metal ferrites obtained in this manner can be used to remove hydrogen sulphide from a gas stream. Based on a Taguchi experimental design, ferrite solid particle and pore size, and the temperature resulting in maximum retention of H₂S by the solid were optimised. Under the optimum conditions, predicted by the method, each gram of ferrite was able to retain 0.274 g H₂S. In addition, a ferrite containing a known lead concentration, obtained by the precipitation method under optimal conditions of pH, temperature and Fe/Pb ratio, was used to study the exothermic H₂S retention reaction. The chemical reaction occurring between the ferrite and the H₂S was investigated by characterisation of the compounds before (Pb_{0.04}Fe_{0.96}^{II}Fe₂^{III}O₄·nH₂O solids composed of Pb_xFe_{3-x}O₄, magnetite Fe₃O₄ and hydrated lead oxide PbO_n·H₂O) and after (PbS, PbSO₄, S, FeS₂ and α-FeO(OH)) the retention process.

Keywords: ferrites, hydrogen sulphide retention, Taguchi experimental design, reaction mechanism

1. Introduction

It is well known that some metals are indispensable for life. Others are inert or innocuous yet some, even at low concentrations, are pollutant showing high toxicity (Sigel *et al.*, 1994) due to their cumulative nature. These may lead to different diseases such as cancer or gastric disorders etc. Other types of pollutants are generated by activities such as combustion, emission of car exhaust fumes and industrial processes. These include particles, sulphur, organic compounds, nitrogen, halogens and radioactive compounds and also provoke several illnesses, particularly respiratory problems. The present study was designed to evaluate a method of removing hydrogen sulphide, a highly toxic and strong smelling air pollutant, from a gas stream.

In a series of previous articles (Barrado *et al.*, 1996a, b, 1998) we optimised a method for the purification of metal-containing waste water which was first described by Tamaura *et al.* (1991). The process is based on the addition of Fe²⁺



ions to the waste water, the alkalisation of the medium to form ferrous hydroxide, and the partial oxidation of Fe^{2+} to Fe^{3+} by air bubbling. This process leads to the formation of a ferrite sludge with magnetic properties and the adsorption and coprecipitation of the metal ions present in the waste water. The properties of these ferrites permits their use in several applications such as toners for laser printings, pigments, magnetic bands, adsorbents etc. (Prieto, 1997).

The possibility of using good performance metal oxide sorbents as desulfurising agents has been proposed in several reports. García *et al.* (1997) investigated the behaviour of different mixed oxides including zinc titanates and zinc ferrites modified with CuO or TiO_2 as hot gas desulfurising sorbents. Li *et al.* (1997) proposed that binary Cu-Cr-O and Cu-Ce-O oxides could serve as regenerable sorbents for high-temperature fuel gas desulfurisation, and Rodríguez *et al.* (1997) examined the reaction of H_2S with chromium, chromia and Au/chromia films grown on a $\text{Pt}(111)$ crystal using photoemission spectroscopy.

In this investigation, ferrites previously obtained by an optimisation process for the purification of waste water containing 15 metal ions (Barrado *et al.*, 1998), were classified according to pore and particle size to be used for the retention of H_2S . Irrespective of the H_2S concentration of the gas stream, a Taguchi parameter design $\text{L}_8(2)^7$ was used to determine the experimental conditions leading to the greatest gas retention by the solid. After establishing that gravimetric and iodometric determinations led to different H_2S retention values, we decided to use a simple solid compound containing only one metal (lead) to establish the mechanism of the ferrite/ H_2S reaction in an attempt to clarify this discrepancy.

2. Experimental

2.1. FERRITE PRODUCTION

The ferrites used in this study were the products of previous optimisation of a method of waste water purification performed in a 5 L reactor (Barrado *et al.*, 1998). A solution containing 3296 ppm of heavy metals (As, Ba, Cd, Cu, Co, Cr, Fe, Mn, Hg, Mo, Ni, Pb, Sr, V and Zn) was purified by means of ferrite formation under different experimental conditions, and in the presence of different amounts of EDTA to simulate the complex anions which may be present in laboratory waste. This process gives rise to 3 types of ferrite differing in pore size determined using a Micrometrics Instrum. corp. model Autopore III 9420 mercury intrusion porosimeter. This instrument permits a working pressure of 0–30 psi (air pressure, pore size 360.0–3.6 μm) and 30–36 000 psi (oil pressure, pore size 6.0–0.003 μm).

The ferrites were milled in a Pascall Engineering Co. Ltd. Machine No. 23098 ball-bearing, and then sieved and separated according to particle size to obtain two fractions (<0.20 mm and >0.30 mm) using a Fritsch Laborgerätebau sieve. The lead ferrite, used here to examine the H_2S /ferrite reaction, was obtained under the

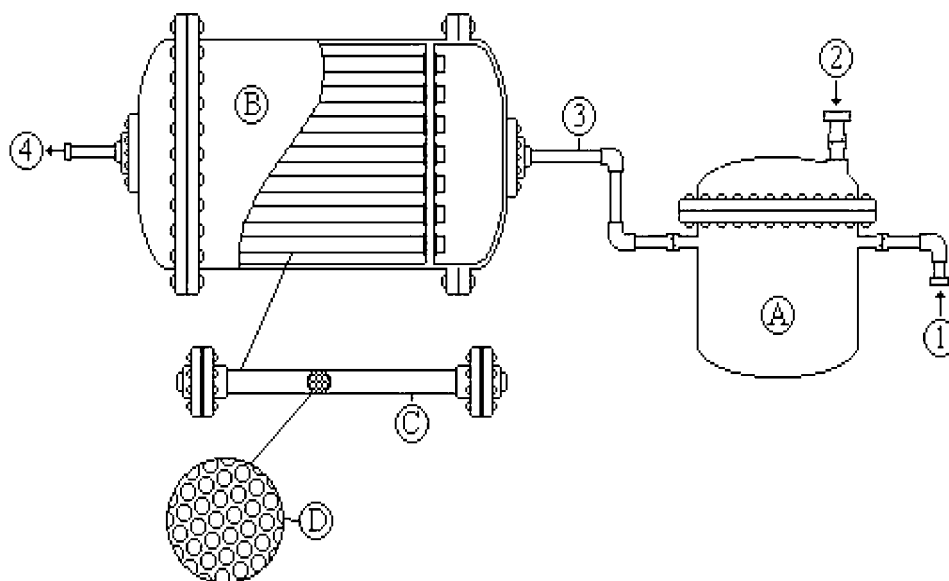


Figure 1. H₂S retention system: A = H₂S generation reactor: 1 = HCl entry; 2 = FeS entry; 3 = H₂S stream. B = H₂S retention vessel: 4 = output. C = Ferrite support tube. D = Solid ferrite.

optimal conditions predicted for the purification process (Barrado *et al.*, 1998). After pulverization to a particle size of 100 μm , a portion was used for characterisation and the rest was introduced into the tubes of the 'retention system'. Pre- and post-retention process samples were appropriately stored until characterisation.

2.2. 'H₂S RETENTION SYSTEM'

The equipment used for the H₂S retention process (see Figure 1) consisted of a glass tube (where the pulverised ferrite is placed) joined to a reactor where hydrogen sulphide is produced by the reaction of ferrous sulphide (FeS) with hydrochloric acid (HCl). A 1.00 g sample of ferrite, weighed to a precision of ± 0.0002 g on an analytical balance (Swiss Quality Model Precisa 125-A), was introduced into the corresponding tube and exposed to a stream of H₂S. Once the solid was saturated with H₂S, indicated by a colour change, the tube was weighed to estimate the quantity of H₂S retained by the solid (by weight difference). The ferrite was then subjected to iodometry in a Kjeldahl Labson Systems distillatory. In brief, HCl is added to an approximate 0.05 g sample, which is heated and distilled in a water vapour stream ($\text{S}^{2-} + 2\text{H}_3\text{O}^+ \leftrightarrow \text{H}_2\text{S} \uparrow + 2\text{H}_2\text{O}$). The distillate is collected in 25 mL of I_3^- ($\text{H}_2\text{S} + \text{I}_3^- + 2\text{H}_2\text{O} \leftrightarrow \text{S} + 3\text{I}^- + 2\text{H}_3\text{O}^+$). Finally, this solution is titrated with sodium thiosulphate ($\text{I}_3^- + 2\text{S}_2\text{O}_3^{2-} \leftrightarrow 3\text{I}^- + \text{S}_4\text{O}_6^{2-}$).

TABLE I
Optimisation experiment: Factors and levels

Notation	Factor		Level 1	Level 2	Level 3
P	Pore diameter	(nm)	123	118	111
T	Temperature	(°C)	25.0	40.0	60.0
D	Particle diameter	(mm)	<0.20	>0.30	–
N	Mass of H ₂ S	(g)	3.03	6.01	–

TABLE II
Experimental L₈(2)⁷ orthogonal array (two-level noise factor) and retained H₂S per 1.00 g of ferrite (H₂SR)

Trial	Control factors and levels			H ₂ SR (g)	
	P	T	D	N1	N2
1	1	1	1	0.2303	0.2703
2	1	2	2	0.1549	0.1453
3	2	1	2	0.2047	0.2222
4	2	2	1	0.2659	0.2027
5	2	2	1	0.2520	0.2158
6	2	3	2	0.0963	0.1820
7	3	2	2	0.1250	0.1035
8	3	3	1	0.1357	0.1950

2.3. OPTIMIZATION OF OPERATIONAL VARIABLES

A Taguchi experimental design (Taguchi, 1991; Ross, 1988) was used to optimise the operational variables of the system leading to maximum hydrogen sulphide removal from the gas stream. The incorporation of this design in the retention system involved the following steps:

- Selection of the output variable. The quantity of H₂S retained (H₂SR) by the solid – determined gravimetrically – was selected as the variable to be optimised, to ensure optimum H₂S removal from the gas stream by the solid ferrite.
- The identification of factors and their interactions affecting the output variable and selection of the levels to be tested: pore diameter, particle diameter, temperature of the gas and mass of H₂S (noise). Pore diameter was known from the optimisation of the water purification/ferrite production process and is affected by the EDTA included as a noise factor to simulate sample vari-

ability (Barrado *et al.*, 1998). This compound is highly chelating and forms very stable complexes with numerous cations, and thus also seems to affect the microstructure of the ferrites formed. These, depending on the solid concentration used, showed pore diameters of 123, 118 and 111 nm (± 2 nm). Particle diameter was determined during the preparation of the solid ferrites, which were milled and sieved to obtain five different solid ferrite fractions. Only the two extreme fractions (<0.20 and >0.30 mm particle diameters) were used for the experiment. The temperature of the gas used was also set at three levels: 25, 40 and 60 °C. The amount of H₂S generated from FeS was used as a noise factor at two levels: 3.0 and 6.0 g. Table I shows the different factors and levels used in the experiments.

- c. Selection of an appropriate orthogonal array. Based on the results of previous studies, an L₈(2)⁷ orthogonal design was employed. This design involves a total of 16 tests consisting of 8 trials, each performed at two noise levels (Table II).
- d. Experiments were performed according to the combinations shown in Table II.
- e. Statistical analysis of data and estimation of signal-to-noise ratio and optimum variable levels.
- f. A confirmatory experiment to check that the conditions, proposed by the design, did in fact lead to maximum H₂S retention.

2.4. ANALYSIS OF LEAD FERRITE BEFORE AND AFTER THE H₂S RETENTION PROCESS

To determine the composition and structure of the lead ferrite before and after use for the removal H₂S, samples (pulverised to a particle size of 100 μ m) were subjected to X-ray diffraction analysis (XRD) using a Philips PW1710 X-ray diffractometer equipped with a Cu anode, an automatic divergence slit and a graphite monochromator. The experimental conditions were: CuK α radiation, 0.154 nm; generator tension, 40 kV; generator current, 30 mA; intensity ratio (α_2/α_1), 0.500; divergence slit, 1°; receiving slit, 0.1; starting angle ($^{\circ}2\theta$), 5; final angle ($^{\circ}2\theta$), 70.

X-ray fluorescence (XRF) determinations were conducted using a Philips PW1840 sequential X-ray fluorescence spectrometer equipped with a Sc-Mo dual anode. Generator tension and current were 80 kV and 35 mA, respectively. The spectrometer was kept at 29.7 °C throughout the experiment, with a type PR gas flux (90% argon and 10% methane) of 0.7 L hr⁻¹. Standard solids were obtained by homogeneously mixing PbO with Fe₂O₃ at ratios of 1, 3, 6, 9 12 and 15% (PbO mass/Fe₂O₃ mass). Samples were prepared by mixing the solid ferrite with lithium tetraborate and lithium bromide and melting the mixture at 1300 °C in a platinum crucible.

A Mettler DSC30 (Mettler, Germany) differential scanning calorimeter (DSC) equipped with a Mettler TC11 processor was used to record DSC curves for the ferrite samples from 0 to 500 °C at a rate of 10 °C min⁻¹ in an air stream of 5 L min⁻¹.

TABLE III
Pooled ANOVA

Source	Pool	Df	S	V	F	S'	rho %
I	[N]	1	0.0218	0.0218	18.8402	0.0206	19.56
P2P3	[N]	1	0.0097	0.0097	8.3830	0.0085	8.07
T1T2	[N]	1	0.0071	0.0071	6.1360	0.0059	5.60
T2T3	[Y]	1	0.0021	0.0021	35.0013	0.0393	37.32
e1	[N]	4	0.0181	0.0045	3.889	0.0150	12.82
e2	[N]	0	0.0000				16.52
Total (Raw)	[-]	15	0.1053	0.0070			

Fourier Transform Infra-Red (FTIR) was performed using a Magna-IRT^M Nicolet 500 spectrometer with KI optics linked to a computer and OmnicC software. Samples were previously ground to prepare a CsI (1:200) tablet.

3. Results and Discussion

3.1. OPTIMISATION OF RETENTION SYSTEM CONDITIONS

Table II shows the design matrix and the quantity of H₂S retained by the solid (H₂SR) in the 16 experiments. H₂SR was gravimetrically given by the difference between the initial ferrite mass and that determined after the H₂S retention process. The data show that the mass of H₂S retained at the different factor levels ranged from 0.096 to 0.270 g per gram of ferrite. It may be deduced by simple visual observation of the table that low temperatures, large pores and small particles lead to optimal H₂S removal. Nevertheless, an analysis of variance (ANOVA) was performed (Table III) to isolate the contribution made by each factor and establish optimum conditions considering the possibility of interaction between factors. It may be observed that a change in temperature level (from level 2 to 3) significantly affects the final signal. The contribution of this variation is 37.3% with remaining factors showing minor contributions compared to the temperature of the gas. This analysis provided an initial combination of optimum values for the control factors (Figure 2a) i.e., P2 (pore diameter) = 118 Å; T1 (temperature of the gas) = 25 °C; and D1 (particle diameter) <0.2 mm. The N (noise) factor showed no statistically significant effect (at the 95% confidence level) on the final result.

However, level N1 gave rise to a slightly lower signal value. The effect of the noise factor was clear: most rapid saturation of the solid ferrite was achieved at the highest H₂S concentration of the gas stream, and highest H₂SR values were

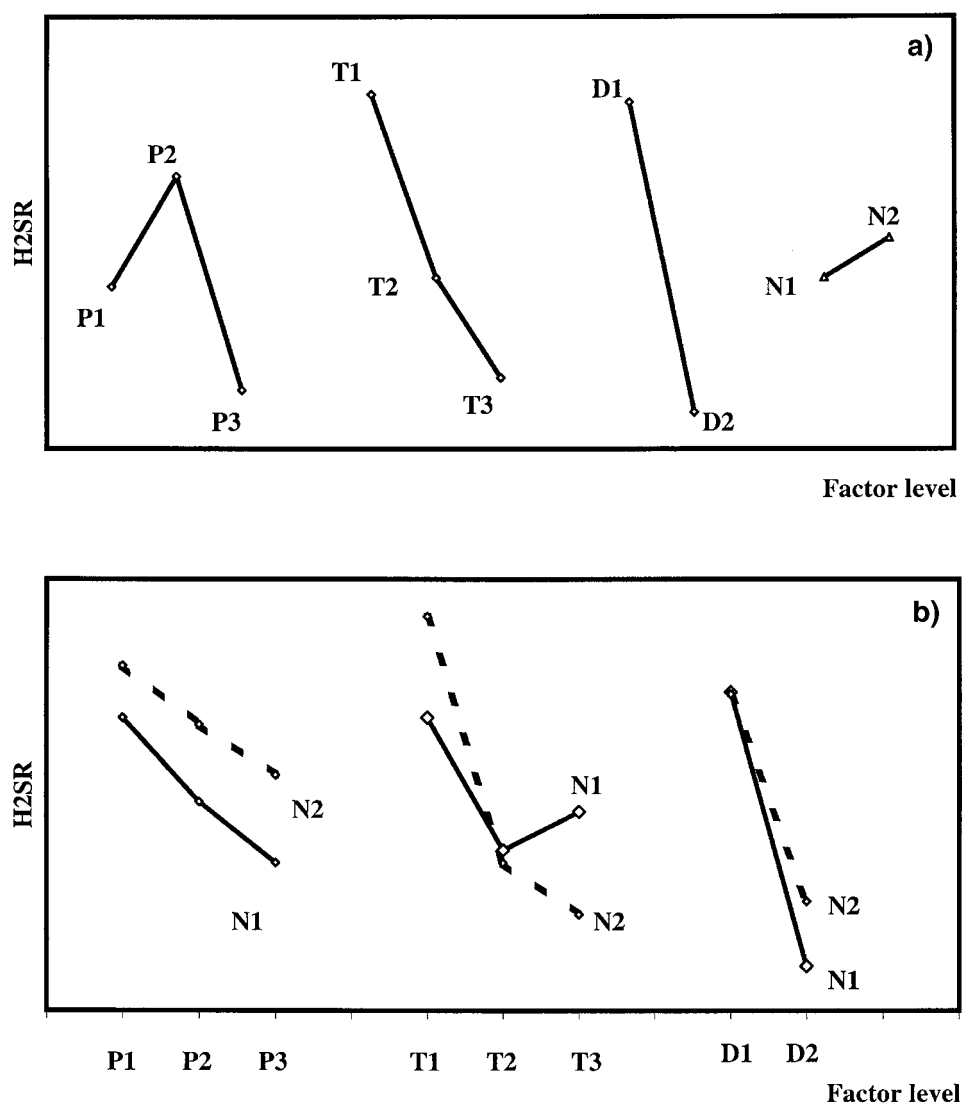


Figure 2. a) Effects of the control factors: P (pore diameter), T (temperature of the gas), D (particle diameter) and the noise factor N (amount of H_2S generated) on the mean response (quantity of H_2S retained, H_2SR). b) Effects of the interactions control factors \times noise factor on the mean response.

obtained using level N2 (noise factor, 6.0 g of initial H_2S). To further analyse this finding, the relationship between the response and the noise level chosen was examined (Figure 2b). This shows the real effect of the noise level on the system signal. Factor P (pore diameter) was identical at each of the noise levels tested. The H_2SR for noise factor N2 was higher than that obtained using noise factor N1 and is easily explained by the higher absorption of H_2S on the solid ferrite when the gas concentration is higher. The behaviour of the gas temperature factor was dependent

on the noise factor level considered. For a noise level of N1, maximum removal of H₂S was achieved at T1. Higher gas temperatures resulted in reduced absorption, although the highest temperature level (T3) yielded a higher H₂SR than T2. At the N2 noise factor level, absorption diminished with temperature leading to enhanced removal at the lowest temperatures. The effect of the noise factor on the signal in terms of the last of the factors considered (D, particle diameter) was invariable: for level D1, a similar amount of H₂S was removed from the gas stream irrespective of the noise factor.

A further analysis of variance was conducted to compare the signal-to-noise ratio (S/N). This permits the evaluation of variation in the response around the mean value due to experimental noise, and the determination of an optimum response with smaller variations which makes the method robust against uncontrollable variability. As H₂SR is a 'higher-is-better' response, the equation employed to calculate the S/N ratio was (Ross, 1988):

$$S/N = -10 \log \left(\frac{1}{N} \sum_{i=1}^N \frac{1}{y_i^2} \right)$$

where N is the number of repetitions in each of the eight trials ($N = 2$) and y_i represents the two experimental values. Pooled ANOVA of the signal-to-noise ratio (S/N) revealed that factor D (particle diameter) contributes to the variability of this ratio by 40.2%, while the contributions made by pore diameter and temperature of the gas were negligible, indicating no significant difference (at the 95% confidence level) between the three pore diameter and three temperature levels tested.

The graphical representation of the effect of control factors on the S/N ratio is very similar to that shown in Figure 2a. Maximum hydrogen sulphide removal showing the least variability, i.e. lowest S/N ratio, was achieved using the following combination of factor levels: P2 (pore diameter), 118 nm; T1 (temperature of the gas), 25 °C; and D1 (particle diameter), 0.2 mm. These optimum conditions confirmed the results of the initial ANOVA.

3.2. APPLICATION OF THE PROCEDURE

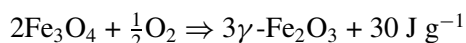
The optimum combination of factors predicted by the model i.e., P₂T₁D₁ (Table II) has not been tested previously. Thus, a confirmatory experiment was conducted under these conditions achieving a removal efficiency of 0.274 g H₂S g⁻¹ ferrite. This value is higher than those obtained using the other variable combinations (see Table II) and confirms the reliability of the model and the ANOVA for the determination of optimum conditions.

3.3. CHARACTERISATION OF THE LEAD-FERRITE SLUDGE BEFORE H₂S RETENTION

As already mentioned, the values of the amount of H₂S retained by the ferrites determined by gravimetry were higher than those provided by iodometry (20 and 5% of the ferrite mass, respectively). To determine the reason for this discrepancy, a lead ferrite sample was prepared under optimum conditions proposed in previous reports (Barrado *et al.*, 1998; Prieto, 1997), and was characterised in terms of chemical composition, crystalline structure, stoichiometry and properties before and after its use in the H₂S retention process.

To determine the actual concentration of Pb (II) and total Fe, 0.100 g of the lead-bearing ferrite was dissolved in 20.00 mL of 35% HCl and diluted to 100.00 mL with deionised water. The ICP-AES determinations of dissolved Pb(II) were $3.49 \pm 0.03\%$ and total Fe was $69.58 \pm 0.03\%$. Fe(II) contents according to potentiometric titration were $22.57 \pm 0.07\%$. The percentages of total Fe (II plus III) and Pb(II) levels of the solid samples directly determined by XRF were consistent with those described above and resulted in the following empirical formula for the lead-bearing ferrite: $\text{Pb}_{0.04}\text{Fe}_{0.96}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4 \cdot n\text{H}_2\text{O}$.

To confirm this stoichiometry, the lead-ferrite was subjected to XRD, DSC and FTIR. Figure 3a shows a representative XRD pattern which indicates that, in addition to a major magnetite (Mgn) phase, there is a series of relatively low intensity peaks, which may correspond to the presence of crystalline phases of hydrated lead oxides. Figure 3b presents the DSC curve of the same compound showing three endothermic and one exothermic peak. The first endothermic peak, recorded from room temperature to 163 °C, is associated with the loss of humidity of the solid. The exothermic peak, from 160 to 255 °C with a maximum value at 238°C, corresponds to the transformation of magnetite to maghemite according to the reaction:



In contrast, the Pb⁺² ion shows a scarce tendency to occupy the octahedral positions of the inverse-spinel structure of the ferrite since its ionic radius is far greater than that of Fe. Consequently, during the ferrite sludge formation process and given the alkaline medium employed, it is possible to predict the formation of hydrated lead oxide according to:



The two smaller endothermic peaks observed, from approximately 254 to 342 °C could therefore correspond to the loss of water of crystallization molecules by the hydrated lead oxide, with a total energy exchange of 33 J g^{-1} which would appear to occur in two very close stages. The presence of the hydrated lead oxides was confirmed by XRD analysis of the solids heated at 340 °C for 4 hr. In the

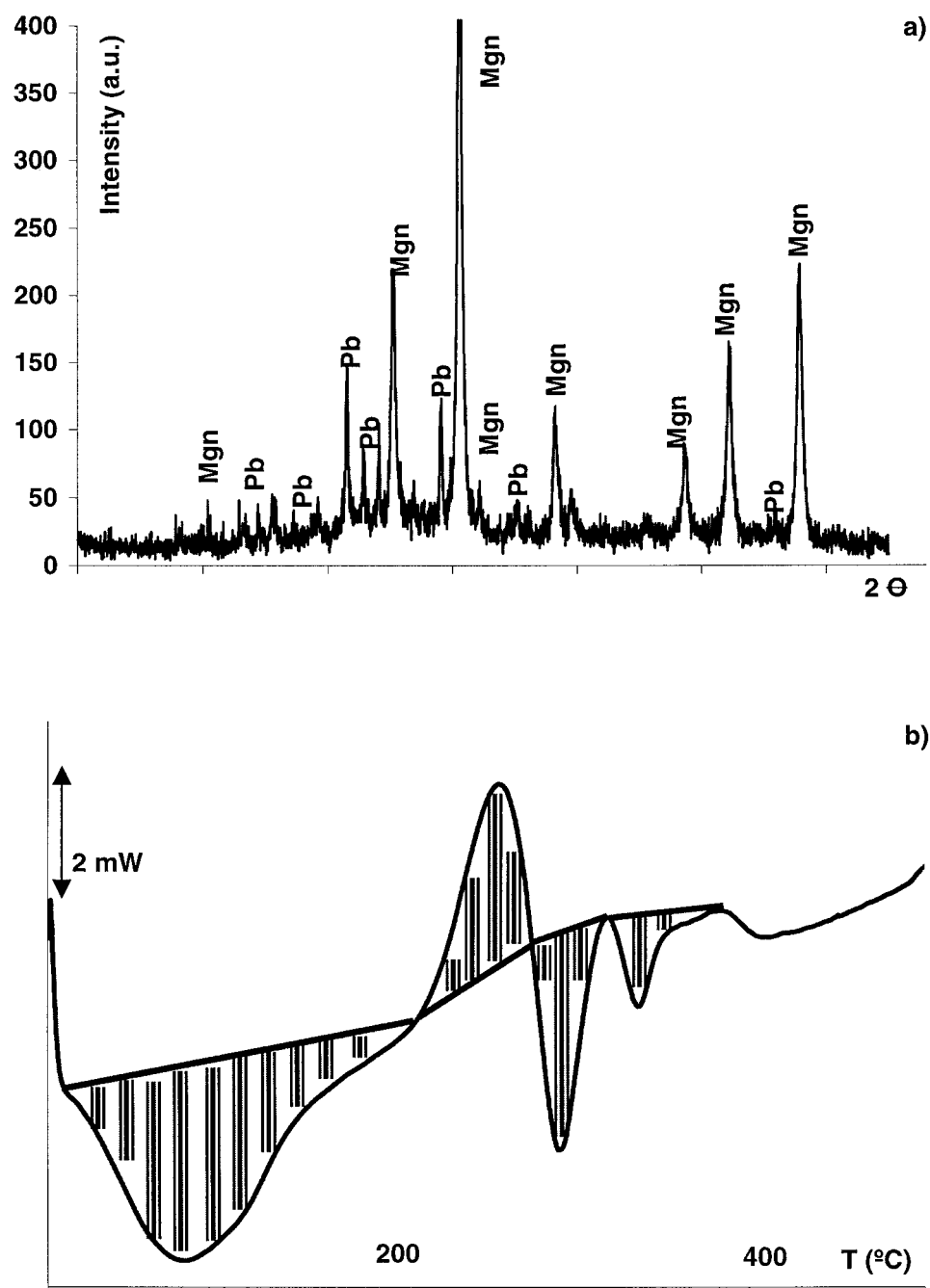


Figure 3. a) XRD pattern of the lead-bearing ferrite. Signals correspond to magnetite (Mgn) and hydrated lead oxides (Pb). b) DSC curve registered from room temperature to 500 °C showing three endothermic and one exothermic peak.

resultant diffractogram it was possible to identify lead oxides corresponding to anhydrous crystalline structures of the type PbO (massicot) or PbO_{1.44} in addition to the maghemite phase (α -Fe₂O₃).

Finally, the FTIR spectra of the compounds, from 300 to 700 cm⁻¹ (Barrado *et al.*, 1999), showed three characteristic bands corresponding to the vibrations: MT-O-MO, MO-O and MT-MO, where MT and MO denote the metal ions occupying tetrahedral and octahedral positions, respectively.

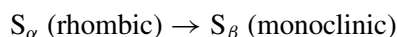
The empirical formula proposed is Pb_{0.04}Fe_{0.96}^{II}Fe₂^{III}O₄·nH₂O, with the solid composed of lead ferrite Pb_xFe_{3-x}O₄, magnetite Fe₃O₄ and hydrated lead oxide PbO·nH₂O.

3.4. CHARACTERISATION OF THE FERRITE AFTER H₂S RETENTION

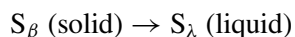
The lead ferrite was used for the retention of H₂S in the solid structure. The reaction which takes place is exothermic and may be experimentally demonstrated because of the increase in the temperature of the glass tube where the ferrite is introduced. When the compound was saturated with H₂S it was subjected to the previous analyses.

Figure 4a shows the XRD pattern of this compound which is considerably different to that of the starting lead-bearing ferrite (see Figure 3a). The results obtained show the existence of different compounds: S (S, orthorhombic) PbS (Gal, galena), PbSO₄ (An, anglesite), α -FeO(OH) (Go, goethite) and FeS₂ (Ma, marcasite). In contrast, the peaks corresponding to magnetite and lead oxides were absent.

The DSC pattern (Figure 4b) shows the presence of several endothermic and one exothermic peak. The first endothermic peak, from room temperature to approximately 90 °C with a total energy change of 2.5 J g⁻¹, is associated with the loss of humidity of the solid. The next two endothermic peaks, from 90 to 145 °C, correspond to S transformations with a total energy exchange of 13.1 J g⁻¹. The first peak, with a maximum at 110 °C, is associated with the temperature of the polymorphic transition:



The second peak, with a maximum at 115 °C, corresponds to the melting point of S according to the transformation:



where S_λ correspond to an S₈ molecule.

A small peak occurs from 145 to 183 °C (total energy exchange 1.5 J g⁻¹) and is related to the different transformations of the liquid phases of the S (S_λ, S_π and S_μ). These molecules occur in different ratios in the melted S, depending on the temperature which causes the chains to split up into shorter chains. Later on, a large

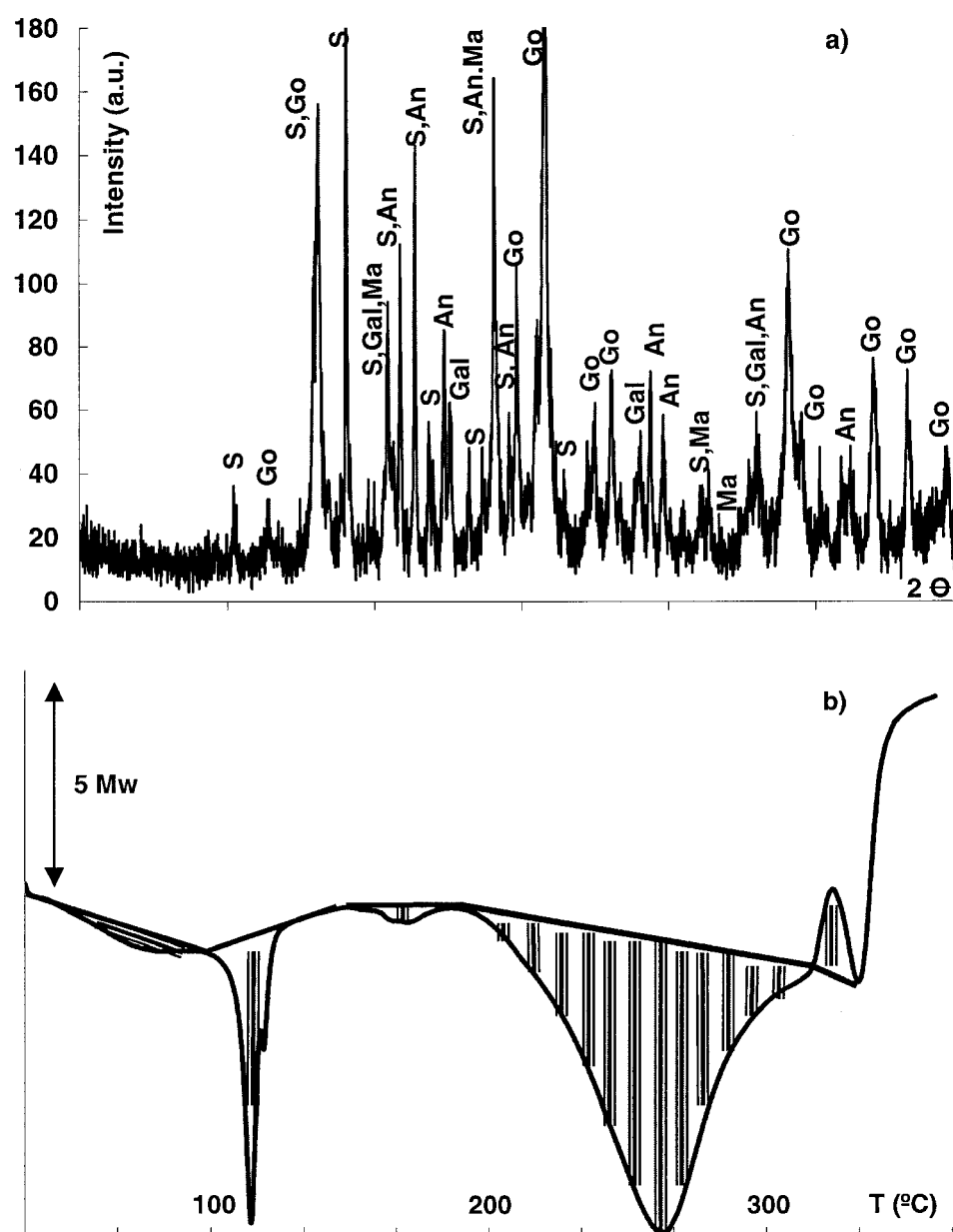
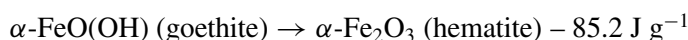


Figure 4. a) XRD pattern of the lead ferrite after saturation with H_2S showing signals corresponding to sulphur (S), goethite (Go), marcasite (Ma), anglesite (An) galena (Gal). b) DSC curve of the same compound showing 5 endothermic and one exothermic peak.

endothermic peak appears from approximately 183 to 310 °C with a maximum at 257 °C. This corresponds to the loss of water of the goethite (probably crystallised) according to the reaction:



Finally, the DSC shows an exothermic peak between 310 and 329 °C, with a maximum at 320 °C, associated with the oxidation of galena to anglesite according to:



To corroborate these transformations, two portions of the compound were heated for 4 hr at 170 or 340 °C and the XRD patterns of the heated solids obtained. Figure 5a presents the XRD pattern of the solid heated at 170 °C showing the presence of the goethite, galena, anglesite and marcasite phases. In contrast, the presence of S is not apparent due to its fusion and later evaporation. In Figure 5b showing the XRD pattern of the solid heated at 340 °C, only the presence of the anglesite, hematite (Hm, $\alpha\text{-Fe}_2\text{O}_3$) and marcasite phases are observed. This is consistent with the transformations goethite to hematite and galena to anglesite previously proposed.

According to these results, a reaction takes place between the components of the lead ferrite and the H₂S of the type:



The PbS and H₂S adsorbed on the surface of the solid – but not the S and PbSO₄ – can be detected and estimated by iodometry. This would explain the difference between the results obtained by each method.

4. Conclusions

The residues produced when heavy metal-bearing water is purified by the ferrite precipitation method can be used to remove H₂S from a gas stream and thus save costs. In the present report, we establish the optimum conditions of particle size, pore size and working temperature permitting the retention of 0.274 g H₂S per gram of residue, regardless of the hydrogen sulphide flow rate. In the process, the iron and metal oxides are transformed into corresponding sulphides and sulphates, with the concomitant production of sulphur. The final product is an inert solid that is environmentally safer for disposal.

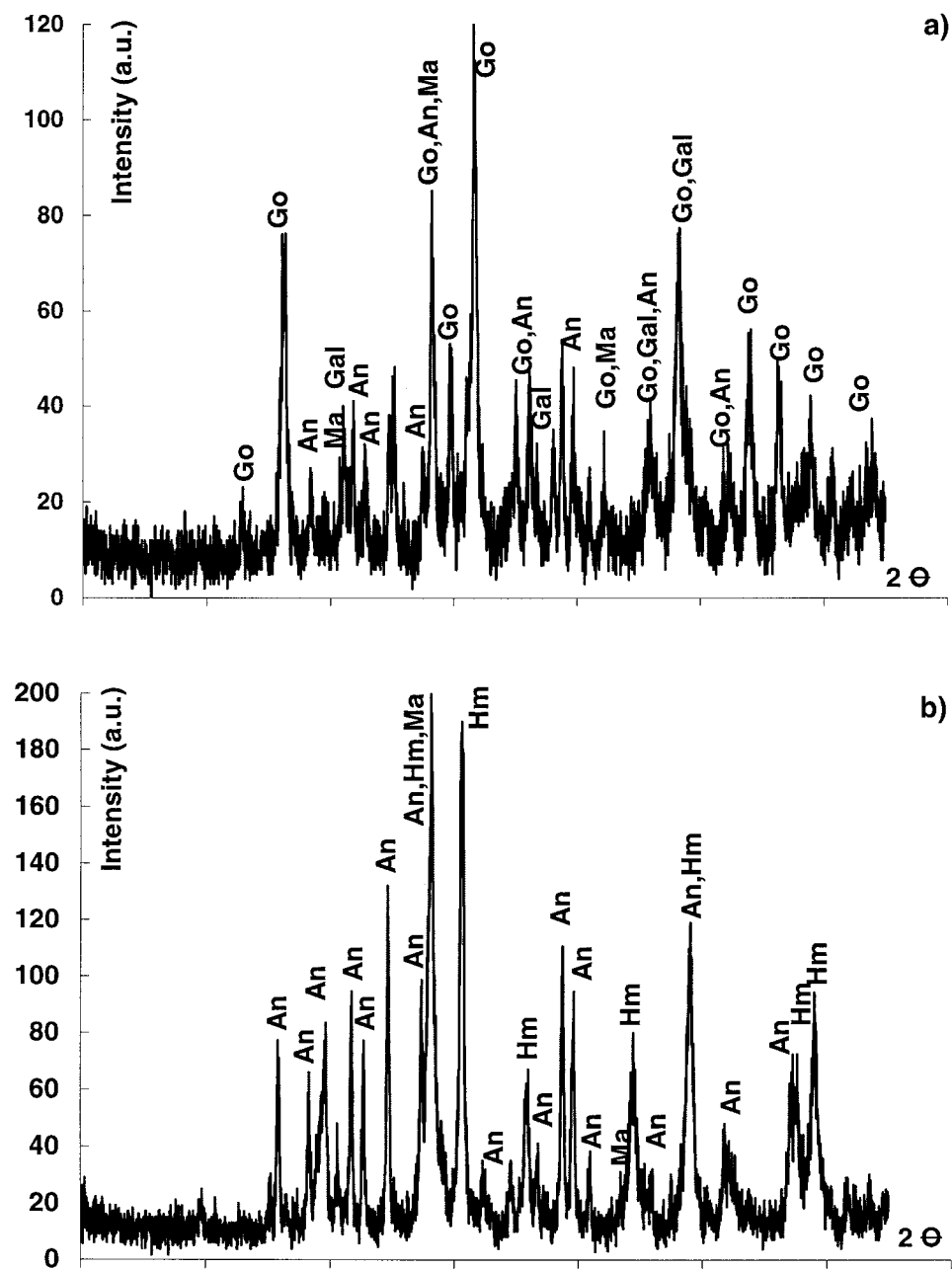


Figure 5. a) XRD pattern of the lead ferrite saturated with H_2S after heating at $170\text{ }^\circ\text{C}$. b) *Id* after heating at $340\text{ }^\circ\text{C}$. Hm denotes the hematite phase.

Acknowledgements

The authors wish to thank the C.I.C.Y.T. (AMB94-0938) for their financial support and A. Burton for her linguistic assistance. F. Prieto also acknowledges the ITEGMA for economic support and the AEI for a post-doctoral grant.

References

- Barrado, E., Vega, M., Pardo, R., Grande, P. and del Valle, J. L.: 1996a, *Wat. Res.* **30**, 2309.
- Barrado, E., Vega, M., Pardo, R., Ruipérez, M. and Medina, J.: 1996b, *Anal. Lett.* **29**, 613.
- Barrado, E., Prieto, F., Vega, M. and Fernández-Polanco, F.: 1998, *Wat. Res.* **32**, 3055.
- Barrado, E., Prieto, F., Castrillejo, Y. and Medina, J.: 1999, *Electrochim. Acta* **45**, 1105.
- García, E., Cilleruelo, C., Ibarra, J. V., Pineda, M. and Palacios J. M.: 1997, *Ing Chem. Res.* **36**, 846.
- Li, Z. and Flytzani-Stephanopoulos, M.: 1997, *Ind. Eng. Chem. Res.* **36**, 187.
- Prieto, F.: 1997, *Depuración de aguas residuales mediante formación de ferritas 'in situ'. Diseño y optimización de un reactor a escala piloto. Evaluación de ferritas*, Ph.D. Thesis, University of Valladolid, Spain.
- Rodríguez, J. A., Chaturvedi, S., Kuhn, M., van Ek, J., Diebold, U., Robbert, P.S., Geisler H. and Ventrice Jr., C.A.: 1997, *J. Chem. Phys.* **107**, 9146.
- Ross, P. J.: 1988, *Taguchi Techniques for Quality Engineering*, McGraw-Hill, New York.
- Sigel, H., Sigel, A. and Seiler, H. G.: 1994, *Handbook on Metals in Clinical and Analytical Chemistry*, Marcel Dekker Inc., New York.
- Taguchi, G.: (1991) *System of Experimental Design*, Vol. I and II. A.S.I.I., U.S.A.
- Tamura, Y., Katsura, T., Rojarayanont, S., Yoshida, T. and Abe, H.: 1991, *Wat. Sci. Technol.* **23**, 1893.