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THERMAL BEHAVIOR OF GALENA ORE IN CHLORINE ATMOSPHERES

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Abstract

The thermal behavior of a purified galena in a chlorine surrounding was determined. The kinetic of the chlorination of galena and the stoichiometry of this reaction between 723 to 973 K (450 to 700°C) were measured by thermogravimetry. The microstructural characterization of the solid residues were determined by SEM, EDXS and XRD. The ΔH_{vap} of the produced lead chloride volatilization was obtained by the application of Clausius-Clapeyron equation considering the process in an equilibrium state.

Keywords: galena ore, kinetic of the chlorination

Introduction

In complex sulfide ores, the galena is almost always present in different concentrations. Sometimes, these concentrations are as low as they do not have an economical importance for metallurgical extraction. Nevertheless, there is a little amount of them in sulfide 'tales', because in the order of some ppm, has a potential degree of environmental contamination.

The exploitation of many complex sulfide ores is not economically feasible using conventional technologies because of their low liberation size. The mineral processing of such materials requires grinding and sequential flotation [1].

Many processes have been developed for the direct processing of lead sulfides to metallic lead. The only ones in commercial operation are the Kivcet and the QSL process. The former is principally a flash smelting process; the latter is in the bath smelting class. Both processes use undiluted industrial oxygen and produced gaseous SO_2 [1].

Due to growing of international concerns about SO_2 emissions from conventional sulfide roasting processes, combined with the demonstrated versatility of metallic chlorides as intermediates in some metal extraction processes [2, 3], and the high reactivity between chlorine and most of sulfides, a renewed interest in the dry chlorination of metallic sulfides has been observed in the recent years.

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An alternative method suitable for treating galena ore could consist of producing sufficiently soluble lead salts from which a very pure metal could be obtained by electrowinning [2, 3]. In most hydrometallurgical processes, sulfuric acid is the main reactant and sulfate solutions chemistry is well known. However, other reactants can be considered, as for example, chlorides. Reaction rate of chlorination applied to galena ore by hydrochloric acid has been measured [4, 5] and the accelerating effect of chlorides in the HCl solutions used for leaching galena is well known [6, 7]. Those studies show that chloride electrometallurgy has attractive advantages *vs.* the conventional sulfates routes. But the following drawbacks must be mentioned: chloride solutions are corrosive, this must be matched by choosing suitable materials for the equipment; cathode deposits of a number of metals show a tendency to be powdery, nodular or dendritic, with a weak sensitivity to additives; solid residues should be thoroughly washed before being disposed as waste for environment protection [7].

Chlorination reactions are able to transform oxides, sulfides, or any other salt depending on its thermodynamic stability, in their respective chlorides. Based on the different reactivity of components of a given ore, and also the different physical properties of metallic chlorides produced by chlorination, it is feasible to separate them and this process is specially suitable for treating ores with low grade as well as complex polymetallic ones.

The reaction rate of lead sulfide with dry chlorine between 772 and 1193 K was measured previously by Landsberg *et al.* [8] at a constant chlorine pressure. The chlorination studies performed by Chen *et al.* was more complete [9]. They were carried out at different chlorine pressures, different flow rates of the gases and the extent of the vaporization loss during the chlorination was taken into account. A two-stage mechanism for the chlorination of a synthetic non-porous PbS pellets was then proposed. During the first stage a clear diffusion control in the gas phase was determined, while during the second stage the diffusion through the liquid lead chloride was the rate determining step [9].

In the present work a natural galena was concentrated and extensively characterized by SEM, EDXS, XRD and INAA, in order to use it in following studies. The chlorination reaction of lead sulfide under conditions of low sample quantities avoiding mixed control and minimizing diffusion control in the gas phase, at constant chlorine pressure, was analyzed. The importance of volatilization of lead chloride and sulfide during chlorination, was taken into account. Also the kinetic of volatilization of lead chloride was determined. The kinetics of the chlorination and evaporation processes was studied by TG and from micrographic and X-ray examinations the solid residues were analyzed.

Experimental

Materials

Argon, 99.99% purity (AGA, Argentina), and Cl_2, 99.8% purity (Indupa, Argentina) were used in this study, powdered materials were lead sulfide ore, purified by a methodology described in a further paragraph.

Procedure

Mass changes occurring during the chlorination of PbS were measured by using a thermogravimetric analyzer (TG), which has been described elsewhere [10]. It consists of an electrobalance (Model 2000, Cahn Instruments Inc.) suitable for working with corrosive atmospheres, a gas line, and a data acquisition system. This experimental set-up has a sensitivity of ±5 μg while operating at 1373 K under a gas flowrate of 91 h^{-1}, measured at normal temperature and pressure. A sample of about 1.5 mg were placed in a quartz crucible and then two procedures were used as follows:

- In a non-isothermal measurement changing the temperature between 298 to 1173 K (25 to 950°C), with a rate of 5 K min^{-1}, in an argon flow of 5 l h^{-1} or and argon–chlorine mixture with a total flow of 7 l h^{-1} at a total pressure of 100 kPa was carried on and mass changes were plotted.
- In an isothermal measurement the sample was heated under flowing Ar and kept for 1 h at the reaction temperature. Chlorine was then introduced and mass changes were measured. Isothermal experiments were performed at flow rates of 7 1 h^{-1} by keeping the chlorine partial pressure constant (35 kPa).

For convenience, mass changes were plotted as $\Delta M/M_i$ (the relation mass change, compared to the total initial mass), which represent fraction mass change. Such plots, i.e. $\Delta M/M_i$ *vs.* t, corrected by apparent mass changes [10], were used for discussing the effect of the kinetic variables on the reaction rate. A hemispherical crucible with a diameter of 0.9 cm was used.

The reactions were stopped at selected conversions and each sample was examined by different techniques. Scanning electron microscopy (SEM) (SEM 515, Philips Electronic Instruments) and Energy dispersive X-ray spectroscopy (EDXS) were used to characterize the morphology and elemental composition of partially reacted solids. A Philips X-ray diffractometer (PW 1710, Philips Electronic Instruments, Inc.) was used to obtain X-ray powder diffractograms from samples and to determine which phases were present. The CuK_α radiation Ni filtered were used. Also, Instrumental Neutron Activation Analysis (INAA) were performed to determine the concentrations of elements in the order of μg g^{-1} present in lead sulfide monocrystals of about 0.1 mm sized, separated under magnifying glass.

Results and discussion

Characterization of mineral

Mineral used in the present study was obtained from a Neuquén's Mine called Tomas Gonzalez, which mineralization analysis indicates the presence of galena, esphalerite, baritine, and quartz.

The rocks were milled in pieces from 5 to 10 mm in size, and a qualitative classification based on different physical characteristics like color, hardness and the streak [11], allowed to separate some of fragments with the highest PbS concentration.

Later, the pieces selected were ground again up to get smaller parts of 1 and 2 mm in size and a new classification by a stereo microscope was then performed. Finally, the pieces separated so were ground in mortar and screened in a sieve, retaining only the material that passed the mesh N° 200, it means particle size below 74 μm. This sample was characterized as is described below and was used in all the kinetics studies.

Figure la shows the particle size distribution of material used in this study. It is possible to see a wide distribution of sizes: the greatest particles are betwen 70 and 80 μm, while an important quantity of them are less that 10 μm, and a lot of submicronic particles can also be observed.

Morphology of galena particles is shown in Fig. 1b, where it is observed, in general, they are cubic or rectangular tetrahedral with steps on faces. Furthermore, the greatest particles present fractures due to the milling process.

EDXS analysis did not allow to determine quantitatively the composition of PbS particles because the lines corresponding to Pb and S were superimposed, but it showed that no other element in a concentration above l atom% was present in them. Also, it was determined the presence of a little amount of another particles composed by (S, Ca), (S, Fe) and (S, Zn).

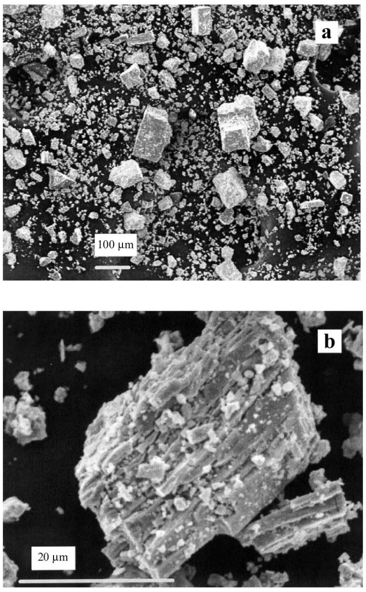
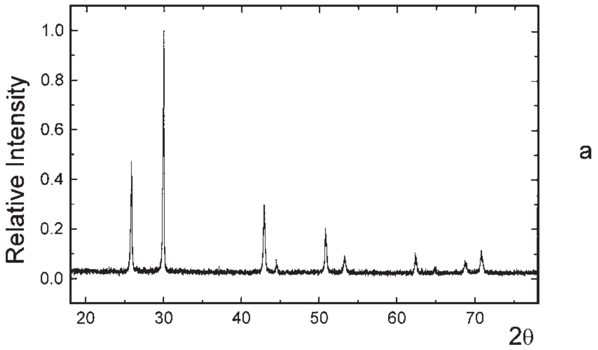


Fig. 1 Distribution of particles size in a galena powder ore (a), Morphology of a galena particle (b)

In the XRD pattern corresponding to this sample (Fig. 2a), the position of different peaks and its relative intensities are in agreement with those corresponding to pure galena, as edited in the Data Base [12]. The diffraction peaks present a gaussian shape with a full width of half maximum equal the instrumental width, denoting that the grain size is greater than 1000 Å. No other peaks are observed in this spectrum, this indicates that impurities present in this ore are lower than 5 wt%.

Neutronic activation analysis (INAA) demonstrated that the mineral has a high purity. In the Table of Fig. 2b, values obtained on two samples taken from the same batch are presented, showing a good homogeneity and confirming previous results. As lead has a very long decay time, it was not feasible to detect it in this way. We consider the elements in the greater proportion appearing in the ore, like sulfides in the



Elements	Sample 1, μg g^{-1}	Sample 2, μg g^{-1}
Antimony	105±11	106±11
Arsenic	3.21±0.28	3.53±0.30
Barium	1000±180	1090±170
Cadmium	25.7±7.7	33.5±7.1
Cerium	<5	<5
Cesium	<1	<1
Zinc	6630±350	6730±380
Cobalt	<1	<1
Chromium	<10	<10
Scandium	<0.1	<0.15
Iron	0.141±0.029	0.141±0.031
Lantanum	<0.2	<0.2
Mercury	3.67±0.65	3.06±0.58
Nickel	<110	<120
Gold	0.0290±0.0073	0.0187±0.0049
Silver	123±8.6	124±12
Samarium	<0.09	<0.09

b

Fig. 2 Qualitative and quantitative characterization of starting galena sample: a – room temperature X-ray diffraction pattern, b – neutron activation analysis case of iron and zinc, and as sulfate for barium because they were determined by EDXS as individual particles. Thus, their concentration calculated as they were in the ore was: ZnS 0.99, FeS_2 0.2 and $BaSO_4$ 0.1 wt%, it is less than 1.5 wt%. The gange of this mineral is probably greater than 1.5 wt% due to the presence of quartz, Si cannot be detected by INAA, but it is specked not to be higher than 5 wt% as indicates the XRD pattern.

Furthermore, among the elements that are present in the order of ppm silver concentration (123 ppm) is highly enough to be of interest, this element is commonly associated with galena.

Chlorination process

Thermal behavior of galena ore in argon atmosphere

The temperature effect on the PbS behavior has to be determined in order to distinguish the changes produced by chemical reactions from those arising from thermal effects. PbS melts above 1391 K (1118°C). The upper part of Fig. 3a shows that its vapor pressure at 873 K (600°C) is 0.15 kPa while at 973 K (700°C) it increases to 1.02 kPa, as it can be seen it changes fast with temperature. The vaporization of PbS in a flow of inert gases due to the continues removal of matter produces the lost of mass sample.

The thermogravimetric curve showed in lower part of Fig. 3b was obtained heating the sample by a non-isothermal procedure. At the beginning, there was a very little mass gain due to changes in the gas density [10] as a consequence of the temperature increase. Above 873 K (600°C), it was possible to detect a mass loss originated by the galena vaporization. At 1073 K (800°C), the slope of curves increased signifi-

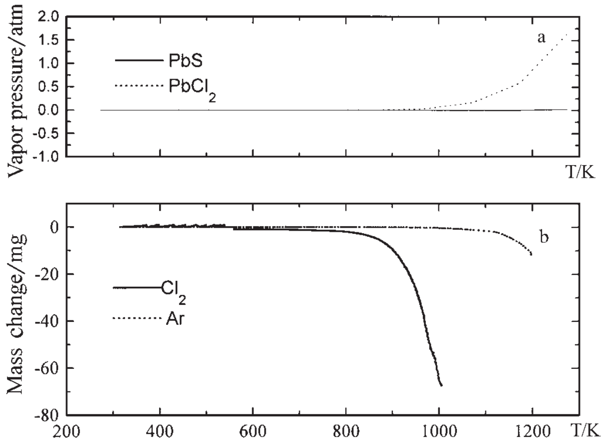


Fig. 3 Non-isothermal heating treatment of galena sample: a – vapor pressure of PbS and $PbCl_2$ compounds at different temperatures, b – thermogravimetry curve in different atmospheres (argon and chlorine)

cantly but at 950°C there was no more mass changes because all PbS had been completely vaporized. The residue analyzed by EDXS indicates the presence of (Ba, S), (Zn, S) (Fe, S) and Si particles and the mass balance show that it is 2 wt% of the initial mass. Considering that pyrite, sphalerite and barium sulfate do not sublime in this temperature range and that the pyrite present in the sample would decompose in pyrrotite, producing a total mass loss of 0.2 wt%, this indicates that the Si particles are about a value of 1 wt%.

The morphology of galena particles after vaporization during 8 h at 1173 K (900°C) is shown at Fig. 4a. The particles maintain its cubic shapes but with smooth faces and rounded edges, some of them are sintered, indicating the high mobility of the atoms into the galena lattice at this temperature. The following experiment was performed in order to determine at which temperature the recrystallization of PbS is important. A sealed-quartz-capsule with the sample at an extreme of it with a temperature of 1173 K (900°C) and a gradient of temperature along it was heated for two days. The reactor was open and the residues were analyzed. It was found at 873 K (600°C) that all the PbS was recrystallized (Fig. 4b) with its typical crystalline habit (Fig. 4c), it means that a pressure of 0.15 kPa is the vapor pressure value enough to generate significant vapor transport with a crystal growth of PbS from this isotropic medium. The residue at 1173 K (900°C) are particles with a composition: (Ba, S), (Zn, S) (Fe, S) and Si, which is similar to that observed in the residue after the non-isothermal thermogravimetry.

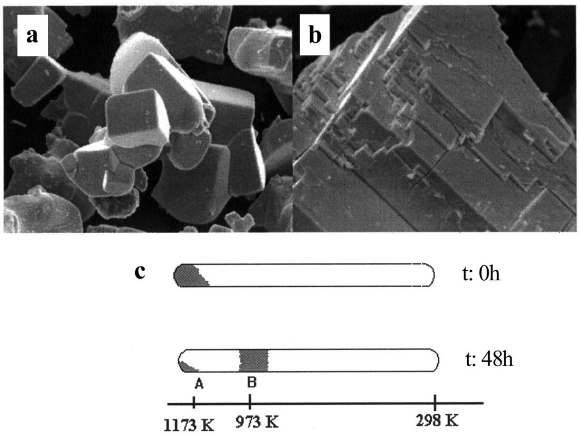


Fig. 4 SEM observations after heating treatment in argon of a galena sample: a – Morphology of the sample after a non-isothermal heating, b – Galena particles recrystallized at 873 K (600°C), c – Sketch of capsule with a gradient of temperature containing galena sample

Previous results indicate that at temperatures above 873 K (600°C) the volatilization process must be taken into account during the mass balance of any other reaction which takes place simultaneously with the thermal process.

Thermal behavior of galena ore in chlorine atmosphere

The direct chlorination of PbS is thermodynamically feasible because the reaction standard Gibbs energy change is negative (ΔG^{o}/kJ mol^{-1}Cl_2= –44.7 –0.10 T), indicating that the process is shifted towards the products and the greater reduction capacity of sulfur on chlorine.

There is information in literature about two solid lead chlorides: $PbCl_2$ and $PbCl_4$, which can be obtained at room temperature, but above 393 K (120°C) $PbCl_4$ is explosive [13, 14]. The thermodynamic data of $PbCl_4$ compound at 100 kPa (1 atm) indicates that the solid phase is metastable at all temperatures, which with a little increasing of temperature transform to the stable gaseous state [15]. The ΔG^{o} [16] values of PbS chlorination reactions represented in an Ellingham diagram (Fig. 4a) are calculated per mol of Cl_2 or per mol of PbS for the two stable compounds ($PbCl_{2(s)}$ and PbCl4(g)), in the first case chlorine is the reactant in defect and PbS in the second one. The negative values of ΔG^{o} indicate that both chlorides are thermodynamically

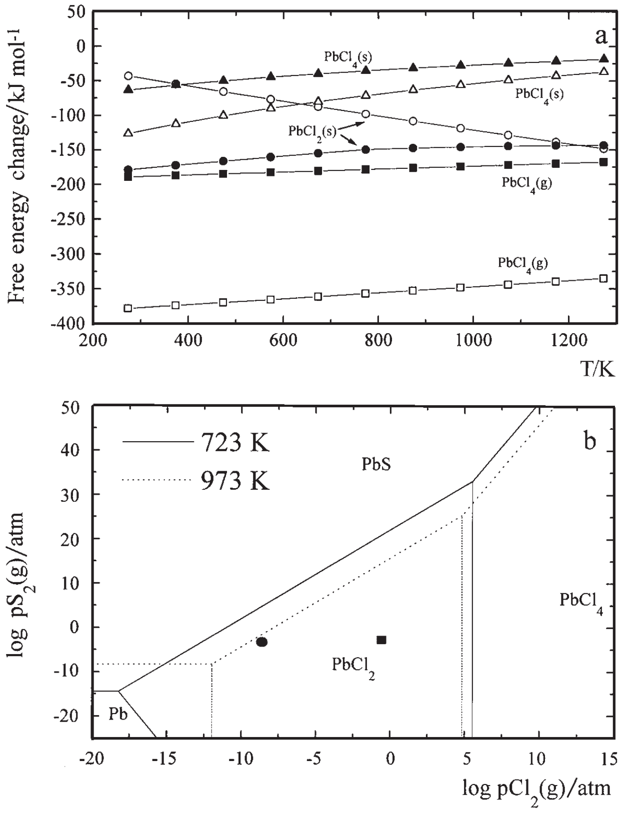


Fig. 5 Thermodynamic analysis of galena chlorination: a – Ellingham's diagram, b – Kellog's diagram at 673 and 1173 K (400 and 900°C). ($PbCl_4$ extrapolated from room temperature). • – Cl_2 in defect, □ – Cl_2 in excess

feasible, but for the $PbCl_{4(g)}$ production the ΔG° has more negative value, meaning that this reaction is the most probable.

In addition, Fig. 5b shows the Kellog's diagram calculated for two temperatures [16]. The partial pressure in equilibrium of sulfur and chlorine calculated by the HSC program considering excess and defect of chlorine are indicated with solid square and solid circle respectively. In both cases, the species in equilibrium is $PbCl_2$ in a condense phase. As in the experimental set-up the maximum total pressure is 100 kPa (1 atm), it was not possible to obtain the conditions needed for the $PbCl_4$ formation which requires much higher partial pressures of Cl_2. Moreover, there was not possible to obtain partial pressures of Cl_2 as low as the system is able to produce metallic Pb.

Then, the stoichiometry of the PbS chlorination reaction between 723 and 973 K (450 and 700°C) may be represented by any of the following equations:

$$PbS_{(s)}+Cl_{2(g)}=PbCl_2+1/2S_{2(g)} \tag{I}$$

$$PbS_{(s)}+2Cl_{2(g)}= PbCl_{4(g)}+1/2S_{2(g)} \tag{II}$$

The aggregation state of $PbCl_2$ depends on the reaction temperature, being solid below 774 K (501°C) and gaseous above 1223 K (950°C). Furthermore, it has a high vapor pressure from 673 K (400°C) as shown in Fig. 3a, much higher than PbS.

When the reaction is taking place, the replacement of sulfur by chlorine produces a mass gain while the vaporization process leads to a mass loss, allowing to follow the reaction kinetic by thermogravimetric analysis.

In Fig. 3b, non-isothermal thermogravimetric curves obtained between 298 to 1223 K (25 to 950°C) show the temperature at which the reaction begins. The chlorination reaction starts at 373 K (100°C) with a mass gain that continues to increase up to 553 K (280°C). At this temperature, the ΔM measured indicates that if the product is the solid $PbCl_2$ all lead sulfide has reacted and it represents about 16% of the starting sample mass. At 553 K (280°C) the curve presents a maximum and above this temperature there is a very little mass loss due to the volatilization of chloride. Although the partial pressure of $PbCl_2$ is very low at this temperature, the chlorine flow enhances the evaporation process and furthermore the reaction $PbCl_{2(s)}+Cl_{2(g)}=PbCl_{4(g)}$ is thermodynamically favorable at this temperature (ΔG° (473 K)= -203 kJ mol^{-1} Cl_2), consequently it is probable that the formation of gaseous lead tetrachloride shifting the reaction to the formation of volatile species. Around of melting point 774 K (501°C), a fast mass loss begins and continues until there is no more $PbCl_2$. After complete evaporation of lead chlorine, only 1 wt% of the initial sample mass remain in the crucible, corresponding to the gange that cannot be chlorinated under those experimental conditions (e.g. quartz).

From non-isothermal experiment results, it can be concluded that the low temperature for the beginning of chlorination reactions is indicative that PbS is very reactive with chlorine, while the mass balance permits to demonstrate that stoichiometry proposed in reaction (1) was the right one at low temperatures.

In a solid-gas reaction different chemical or mass transport processes may become the rate-determining step (RDS). Then, in order to study the intrinsic reaction mechanism it is necessary to accelerate the transport processes. By increasing the total flow of gas, the transport in the gas phase accelerates, and in a previous work [17] it was determined that, for our experimental set-up, the diffusion in the gas phase is $2.5{\cdot}10^{-8}$ mol s^{-1} Cl_2 to a sample similar to that used in the present work. This magnitude corresponds to the diffusion of Cl_2 through the gaseous phase, which not only depends on the nature of solid, but it is directly related with the kind of thermogravimetric set-up, the shape of crucible, the rate flow, etc. In the case of experimental TG used for this study, it was evaluated that when the reaction rate is higher than

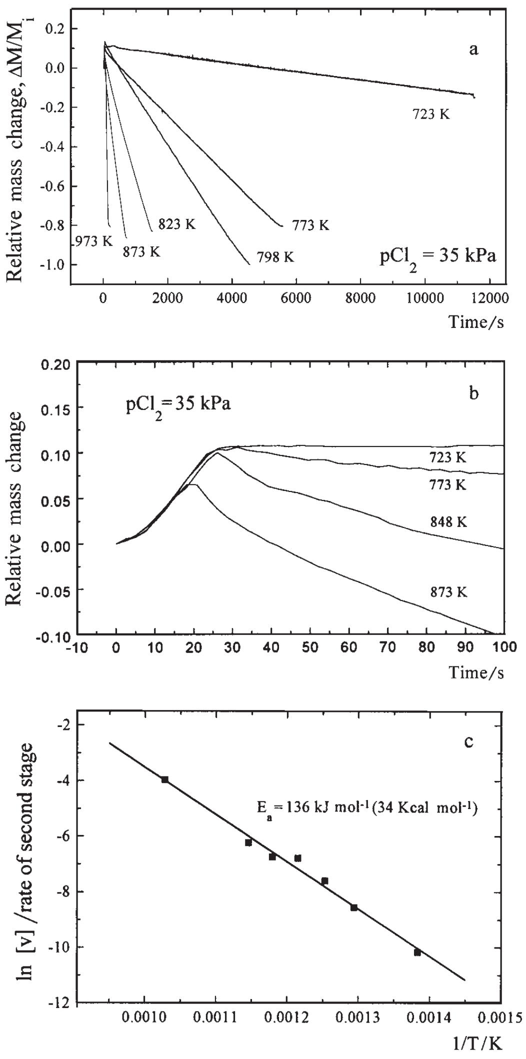


Fig. 6 Isothermal thermogravimetry curves at different temperatures (a), TG curves during the first seconds of the reaction (b), activation energy (E_a) calculated from ln*v* *vs.* 1/*T* plot (c)

$2.5 \cdot 10^{-8}$ mol s^{-1} Cl_2, it is controlled by the transport in the gaseous phase. Then, in the following experiments the total flow used was high enough to ensure that the diffusion in the gas phase did not become RDS.

Another important mass transport phenomenon to take into account is the diffusion through the porous of solid or in the liquid bed, and in order to produce the reaction with a chemical or a mixed control the effect of quantities of material have to be minimized. The effect of mass is possible to eliminate by decreasing sufficiently the quantities of mass until there is no change in the rate of the process [18].

In Fig. 6a, the isothermal thermogravimetric curve of PbS chlorination at 778, 823 and 873 K (505, 550 and 600°C) show that, during the first seconds, a fast mass gain is observed up to reach a maximum, and it is followed by a mass loss. Three curves with different initial masses at 778 K (505°C) were obtained. The rate of the fast mass gain was the same in any case, but the mass loss process was practically invariable below 3 mg. Therefore, in the subsequent experiments an initial mass of 1.5 mg was used, which is the minimum quantity easy to handle.

In Fig. 6b, a detail of the chlorination reaction during the first seconds at 778 K (500°C) is shown, the ΔM calculated, taking into account the stoichiometry already presented for the production of $PbCl_2$, is l6 wt% and the ΔM values determined experimentally is 12 wt%. Moreover, the ΔM are very close to those values calculated if whole PbS is transformed to $PbCl_2$ with a lost of mass due to the chloride vaporization. In order to avoid an overlapping of both processes the reaction rate was calculated during the first seconds and was extrapolated to zero time.

Consequently, the process may be interpreted as occurring in two stages. During the first 200 s, the total chlorination of PbS is produced with a net mass gain, the chlorination rates at the beginning of the reaction present in Table 1 ($2.6 \cdot 10^{-8}$ mol s^{-1} Cl_2 at 500°C and $2.5 \cdot 10^{-8}$ mol s^{-1} Cl_2 at 600°C) are as high as those calculated for a process controlled by the mass transfer of chlorine in the gaseous phase (ca $2.5 \cdot 10^{-8}$ mol s^{-1} Cl_2) [17]. Consequently, it was not possible to study the intrinsic kinetic of the PbS chlorination in the present experimental conditions.

In the second stage, the process occurs with a net mass loss, probably due to the volatilization of $PbCl_2$ which depends markedly on the amount of material, but if it is less than 3 mg, the rate of process does not depend on the sample quantity, assuring that the transport of chlorine in the bulk of sample is so fast that it does not become the controlling step. Therefore, the following important characteristic may be pointed out: the slopes of the mass loss curves do not change as long as the reaction proceeds, showing that the process has always the same exposed area and giving another evidence that the second stage is a volatilization process.

The rate of an evaporation process depends on temperature. By using the same amount of sample (about 1.5 mg), the rate of process at different temperatures was determined. The rates of isothermal curves from 723 to 973 K (450 to 700°C) were measured and shown in Table 1, expressing them in mol of chlorine per s in order to compare these values with those determined in a pervious study on the chlorination of hematite, which were performed in the same experimental set-up [17]. In that study, it was determined that rate process values in the order of $2.5 \cdot 10^{-8}$ mol s^{-1} Cl_2 are indicative of a mass transport in the gaseous phase as RDS, values less than $2.5 \cdot 10^{-8}$ mol s^{-1} Cl_2 suggest that the reaction has a mixed control and when the rate value is less than 1.10^{-9} mol s^{-1} Cl_2, it is apparent that the transformation process is the slowest.

At 973 K (700°C) the first stage was not observed, which is a consequence of the high vapor pressure of $PbCl_2$ the evaporated amount is greater than the condensed chloride.

Comparing these values with those presented in previous work [17], it is possible to conclude that up to 973 K (700°C) the evaporation process is not controlled by the transport in the gaseous phase, if the same diffusion coefficients in the gaseous phase are assumed for chlorine and any other chlorides. As the melting point of $PbCl_2$ is 774 K (501°C), the mass loss observed at lower temperatures is related with the sublimation of the solid chloride.

Table 1 Reaction rates of the first and second stages of the chlorination at temperatures from723 and 973 K (450 and 700°C)

T/K (°C)	First stage rate, v_1	Second stage rate, v_2
	mol s^{-1} Cl_2	
723 (450)	$3.6 \cdot 10^{-8}$	$1.7 \cdot 10^{-10}$
773 (500)	$2.6 \cdot 10^{-8}$	$6.7 \cdot 10^{-10}$
798 (525)	$2.5 \cdot 10^{-8}$	$2.0 \cdot 10^{-9}$
823 (550)	$2.2 \cdot 10^{-8}$	$4.7 \cdot 10^{-9}$
848 (575)	$3.0 \cdot 10^{-8}$	$4.0 \cdot 10^{-9}$
873 (600)	$2.5 \cdot 10^{-8}$	$8.2 \cdot 10^{-9}$
973 (700)	–	$7.8 \cdot 10^{-8}$

The low values obtained for mass loss rates in the range of 778–973 K (505–700°C), as well as the fact that they do not depend on the quantity of sample for masses less than 3 mg, are indicating that the process is not controlled by the mass transfer, neither through the gaseous phase nor through the sample mass.

Taking into account that the evaporation rate depends only on the temperature for a given expose area, it may be expressed as follows:

$$V_{\mathrm{evap}}=kP_{\mathrm{vap}} \tag{1}$$

On the other hand, the Clausius-Clapeyron equation for an evaporation process in equilibrium is:

$$\ln P_{\mathrm{vap}}=-\Delta H/RT \tag{2}$$

Replacing P_{vap} by the V_{evap} and re-arranging the terms:

$$\ln V_{\mathrm{evap}}=-\Delta H/RT+C \tag{3}$$

In Fig. 6c, the graphic of ln$v$ *vs.* $1/T$ is presented, where v is the rate of the mass loss process. As it can be seen, a good lineal fitting was obtained, with a slope of

140 kJ mol^{-1} (35 Kcal mol^{-1}), that is very closed to the value of ΔH for the volatilization of $PbCl_2$ liquid.

These results show that the volatilization process is controlled by the evaporation step. The evaporation rate (number of mol per s and per unity of area), depends only on the system temperature, and, if the following mass transfer stages are quick enough, it must be equal to the condensation step, in order to be proportional to the partial pressure for fitting the CC equation. The last agreement indicates that the volatilization process occurs under equilibrium condition.

Analysis of chlorination residues

With the aim to obtain more evidence about the complete chlorination of PbS during the mass loss portion of thermogravimetric curve, a new chlorination experiment was performed at 543 K (270°C). The thermogravimetric curve at 543 K (270°C) shows only the process of mass gain, because the mass losses cannot be detected at this very low partial pressures of both lead compounds (PbS and $PbCl_2$) at this temperature, the maximum mass gain observed was 16% of the initial mass sample. The XRD spectrum in Fig. 7a shows only the peaks that correspond to $PbCl_2$, indicating that all PbS was chlorinated and the only phase formed was lead dichloride. Additional evidence was obtained by SEM observations and EDXS analysis.

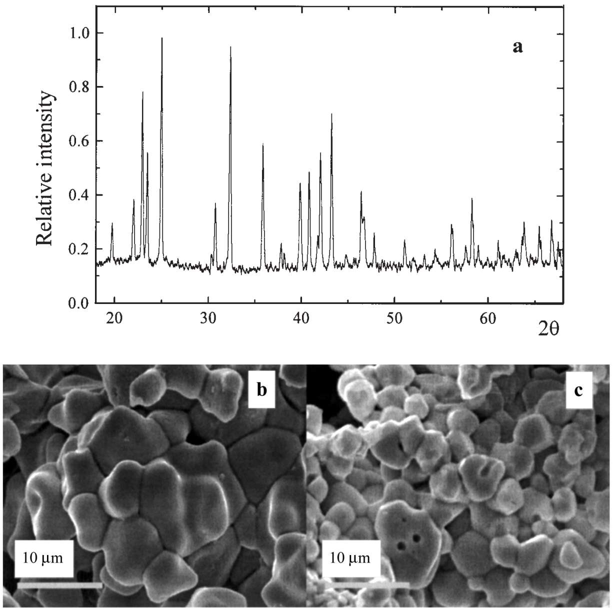


Fig. 7 Microstructural characterization of solid residues after chlorination at 543 K (270°C). (A) X-ray diffraction pattern, (b and c) Morphology of $PbCl_2$ particles

Morphology of those residues were completely different from the starting sample, as it can be seen in Figs 7b, c. In the solid sample, grains of about 5 to 10 μm size are join together by grain boundaries, indicating the high mobility of atoms at this temperature, which is in accordance with the Tammann temperature of $PbCl_2$ 523 K (250°C). In Table 2 the composition in difference points of the surfaces of those grains is presented, the average atomic percentage corresponds to the atomic relation in the formula of $PbCl_2$. The latter one is an important evidence demonstrating that the only chloride formed was $PbCl_2$. Furthermore during the mass gain the whole chlorination of PbS was produced.

Table 2 Quantitative analysis by EDXS on different particles after complete chlorination at 270°C

Particle	Pb/	Cl/
	atom%	
1	32	68
2	35	65
3	33	67
4	30	70
5	31	69
6	31	69
7	29	71
8	32	68
9	31	69

The microstructure of chlorinated residues obtained at higher temperatures 723 K (450°C) changes markedly: the grains have considerably grown, duplicating dimensions were observed at low temperature, they are faceted and the grain boundaries are sharply evident. An inside detail of Fig. 7c shows a very porous matrix, indicating the presence of volatile species during its formation, probably it is a consequence of the gaseous sulfur produced during the chlorination process. Furthermore, the residue of chlorination at 823 K (550°C) completely melted and adhered to the wall of crucible.

Conclusions

It was possible to obtain a very pure galena from a complex ore and to extensively characterize its microstructure.

973 K (700°C) was defined as the temperature at which the PbS volatilization is important. Then the temperature and equilibrium pressure of crystal growth under the present experimental conditions were obtained.

The high reactivity of chlorine with PbS from room temperature does not let us study the intrinsic kinetic of the chlorination, but it was possible to establish the stoichiometry of the reaction and the reaction occurs through a mechanism kinetically controlled by the diffusion in the gas phase.

The volatilization process is uncoupled in time from the chlorination one. Through the determination of the rate of mass loss it is possible to measure the ΔH of volatilization of $PbCl_2$. The lattter one indicates that this process occurs in equilibrium and that the low degree of impurities present has no influence on the properties of the chloride obtained.

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