Journal of Thermal Analysis and Calorimetry, Vol. 86 (2006) 2, 393–401

THERMAL AND XRD ANALYSIS OF EGYPTIAN GALENA

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Galena is the principal ore mineral for lead industry and the production of lead and its alloys. The industrial processing of galena includes its oxidized roasting to lead oxide, followed by reduction smelting of lead oxide agglomerate with coke in the blast furnace to commercial lead.

The present work reports a thermal analysis study of oxidized roasting of Egyptian galena using a derivatograph. The reaction products were identified microscopically and by using a Siemens Crystalloflex diffractometer.

On roasting of galena (heating in the air flow), its oxidation to lead sulphate was shown by a wide and small exothermic DTA peak at 460°C. The reaction between galena and lead sulphate, produced $PbSO_4{\cdot}PbO$ at 580°C, is shown by a small exothermic peak. A large and sharp exothermic tripple maximum at 730, 740 and 765°C was due to the intensive oxidation of galena, accompanied by an increase in mass (TG). This mass increase is attributed to the formation of different sulphates. The mass loss is observed at temperature higher than 900°C due to the dissociation of the sulphates to lead oxide and evolution of sulphur dioxide.

The standard free energy ($\Delta G°$) and equilibrium constant (K) of the reaction of oxidation of galena to lead oxide at 800°C are -167.102 kcal mol^{-1} and $1.09{\cdot}10^{34}$, respectively. These values reflect the irreversibility of the reaction.

The products of the oxidized roasting of galena are different, depending upon the temperature of roasting such as anglesite at 300°C, basic lead sulphates of specified compositions: ($PbSO_4{\cdot}PbO$ at 600°C, $PbSO_4{\cdot}2PbO$ at 800°C and $PbSO_4{\cdot}4PbO$ at 900°C) and lead oxide at 1000°C.

Keywords: *galena roasting, thermal analysis, thermodynamics, XRD*

Introduction

Galena (lead sulphide) is the principal ore mineral for the lead industry and the production of lead, alloys and its compounds, which are used in different fields of industry mainly accumulators, atomic energy, ceramic glasses and glazes, pigments and chemical industry.

Several methods are used for the industrial processing of galena for production of lead and its compounds [1–16, 18–20]. These include pyrometallurgical and hydrometallurgical methods. The pyrometallurgical methods include the oxidized roasting of galena followed by the reduction smelting. The reaction smelting is based on the roasting of galena in reverberatory furnace at 500–600°C and its partial oxidation to lead oxide and sulphate. This is followed by smelting of galena and lead oxide and sulphate at 850°C with the production of lead. Replacement smelting of galena is carried out in blast furnace at 1200°C with addition of iron powder to the charge for replacement of lead. The hydrometallurgical methods are based on preliminary chlorination or sulphatization roasting of galena. Chlorination roasting of galena is carried out for galena in a mixture of coal and sodium choride or using chlorine with the formation of lead chloride. Sulphatization roasting of galena leads to its conversion to lead sulphate. Then, the roasted galena concentrate is leached with a solution of sodium chloride or sodium and calcium chlorides. This is followed by purification of solutions and precipitation of lead by addition of lime (calcium hydroxide) and the reduction smelting of lead oxide.

The main industrial method of processing of galena is its oxidized roasting in air atmosphere [1, 5–11, 15, 17, 20]. This method is based on the oxidation of galena to lead oxide, followed by its reduction smelting in presence of coal. Agglomeration roasting of galena is carried out in agglomerated machine in two stages. The first stage is at 850–900°C, for the removal of most sulphur (6–7% S remain). The second stage includes grinding of the product and its roasting at 1000–1100°C, at which complete oxidation of sulphides and decomposition of sulphates are attained and the formation of lead agglomerate. The roasting is followed by the reduction smelting of lead agglomerate with coal in blast furnace at 1250–1300°C to commercial lead, which is directed to purification processes for the removal of impurities.

Galena was reported [1–6, 8, 11, 20–23, 25] to display a variable thermal behaviour, depending on the conditions of heating. In vacuum, a marked sublimation of galena is observed at high temperatures (at 980 and

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1388–6150/$20.00

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995°C, the vapour pressures are 12 and 17 mm Hg, respectively) and its melting at 1120–1135°C.

In air atmosphere, galena oxidizes during slow roasting at temperature lower than 500°C with the formation of mainly lead sulphate. The lead sulphate resulted reacts with galena with the formation of lead oxide. At higher temperature of roasting of galena (1000°C), lead oxide constitutes the main composition of the end product, due to the dissociation of the lead sulphate and basic sulphates resulted. Lead sulphate formation is remarkably observed during oxidation of galena at 200–300°C, but the process is slow. Under roasting conditions, galena weakly dissociated at high temperatures and the dissociation pressures at 900 and 1000°C are 0.011 and 0.126 mm Hg, respectively.

Lead sulphate is unstable at high temperature. It begins dissociation in air at 637°C. Its intensive decomposition takes place at 705°C with the formation of basic lead sulphates, which at 900–950°C converts to $PbSO_4 \cdot 4PbO$ before being completely desulphurized to lead oxide at higher temperature. Lead sulphate melts at 1080–1170°C [8, 11, 20–23, 25].

Lead oxide melts at 883°C and boils at 1470°C. Its remarkable vaporization is observed at 800°C and this increases at temperatures higher than 950°C. (Vapour pressure is more than 3 mm Hg and at the boiling point reaches 650 mm Hg). The temperature of dissociation of lead oxide is higher than 2000°C [1–3, 8, 11, 20–23, 25].

The present work illustrates a differential thermal analysis and X-ray diffraction study of the oxidized roasting of Egyptian galena using a derivatograph.

Experimental techniques

This research was carried out with galena separated from Um Gheig mineralization, Eastern Desert, Egypt. Galena is lead grey in handspecimens, having a greyish black streak, a metallic luster, perfect cubic cleavage, low hardness and high specific gravity. In polished sections, galena is distinguished by bright white colour, high reflectivity, perfect cubic cleavage, showing triangular pits along the cleavage lines and its crystallization in cubic system.

The X-ray diffraction pattern of the galena sample (Fig. 1) shows only the characteristic peaks of galena; no mineral impurity was detected. The X-ray peaks of galena are well-defined, narrow and intense, suggesting good crystallinity, and their data are consistent with those given in the ASTM index. The chemical composition of the processed galena is given in Table 1.

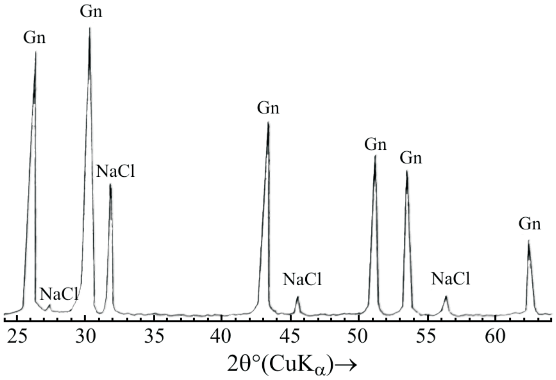

Fig. 1 X-ray diffraction pattern of galena; (*Gn*)

Procedure

Galena was processed by repeated grinding in an automated agate mortar, followed by sieving until all the powder passed through 0.125 and 0.06 mm sieves. Finally, the galena powder was ground with a pestle and mortar for 1 h to achieve homogeneity.

Apparatus

Experiments of galena roasting were carried out using ceramic crucibles heated in an electrical furnace in air current with the removal of sulphur dioxide, which resulted from the oxidation of galena. The temperature was regulated automatically with an accuracy of ±5°C.

The thermal analysis study of oxidized roasting of galena was carried out with the MOM derivatograph [24]. This apparatus records simultaneously four curves; the change of temperature of the sample (*T*), differential thermal analysis (DTA), thermogravimetric analysis (TG) quantitatively in milligrams, and the derivative thermogravimetric curve (DTG) on a single sample under controlled conditions.

The parameters during the test were as follows: ceramic crucible; inert material, aluminium oxide. Mass of sample 187–200 mg; temperature range ambient up to 1000°C; in air atmosphere; heating rate 10°C min^{-1}. The DTA and temperature measuring thermocouples were Pt–Pt/Rh. The atmosphere was air and sulphur dioxide was removed as formed.

Table 1 Chemical composition of galena

Element	Pb	Zn	Fe	Cu	Ca	Mg	Al	Si	S
Content/%	86.21	0.41	0.11	0.04	0.04	0.07	0.02	0.12	12.96

Phase identification

The phases of the products of galena roasting were identified by X-ray diffraction analyses using a Siemens Crystalloflex diffractometer. The finely ground product of roasting was mixed with sodium chloride as a standard. Its peaks at $2\theta=31.38°$ and $45.44°$ were used for corrections. Nickel-filtered copper radiation was used. The exposure time was 1 h. Intensities were collected to a maximum $2\theta= 80°$. The sensitivity of the experiment was $4\cdot10^4$ imp/min and the statistical error was 1.5%.

Determination of thermodynamic constants

Before the thermal analysis study of galena roasting an attempt was done to calculate the thermodynamic constants of its reactions of oxidation. The thermodynamic data given in Table 2 were used in the calculations [17, 20, 26, 27].

Slow oxidized roasting of galena

The reaction may be represented as:

$$2PbS+3.5O_2 \rightarrow PbO+PbSO_4+SO_2 \qquad (1)$$

The standard free energy of the reaction ($\Delta G°$) at 800°C is:

$$\Delta G^{\circ}_{reaction}=\Delta G^{\circ}_{PbO}+\Delta G^{\circ}_{PbSO_4}+\Delta G^{\circ}_{SO_2}-2\Delta G^{\circ}_{galena}-3.5\Delta G^{\circ}_{O_2}$$

$$=-33.056-151.205-72.579+2\cdot22.084+0.00 \qquad (2)$$

$$=-212.672\ \text{kcal mol}^{-1}$$

The equilibrium constant of the reaction (K) may be calculated from the Eq. (3) relating to 800°C:

$$\Delta G°=-RT\ln K$$

$$\log K=\frac{-\Delta G°}{4.57562\cdot1073}=\frac{212672}{4909.64}=43.3172 \qquad (3)$$

$$K=2.08\cdot10^{43}$$

Fast oxidized roasting of galena

The reaction may be represented as :

$$3PbS+5O_2 \rightarrow 2\ PbO+PbSO_4+2SO_2 \qquad (4)$$

The standard free energy of the reaction ($\Delta G°$) at 800°C:

$$\Delta G^{\circ}_{reaction}=2\Delta G^{\circ}_{PbO}+\Delta G^{\circ}_{PbSO_4}+2\Delta G^{\circ}_{SO_2}-3\Delta G^{\circ}_{galena}-5\Delta G^{\circ}_{O_2}$$

$$=-2\cdot33.056-151.205-2\cdot72.579+3\cdot22.084+0.00 \qquad (5)$$

$$=-296.223\ \text{kcal mol}^{-1}$$

$$\log K=\frac{296223}{4.57562\cdot1073}=60.335 \qquad (6)$$

$$K=2.16\cdot10^{60}$$

Formation of lead sulphate

The reaction of lead sulphate formation during oxidized roasting of galena may be represented as:

$$2PbO+2SO_2+O_2 \rightarrow 2PbSO_4 \qquad (7)$$

The standard free energy of the reaction ($\Delta G°$) at 400°C:

$$\Delta G^{\circ}_{reaction}=2\Delta G^{\circ}_{PbSO_4}-2\Delta G^{\circ}_{PbO}-2\Delta G^{\circ}_{SO_2}-\Delta G^{\circ}_{O_2}$$

$$=-2\cdot185.603+2\cdot42.662+2\cdot71.959+0.00 \qquad (8)$$

$$=-141.964\ \text{kcal mol}^{-1}$$

$$\log K=\frac{141.964}{4.57562\cdot673}=46.1013 \qquad (9)$$

$$K=1.26\cdot10^{46}$$

Oxidized roasting of galena to the oxide

The reaction of oxidized roasting of galena to lead oxide may be represented as:

$$2PbS+3O_2 \rightarrow 2\ PbO+2SO_2 \qquad (10)$$

The standard energy of the reaction ($\Delta G°$) at 800°C:

Table 2 Thermodynamic data used in calculations [20, 26, 27]

Temperature/°C	$-\Delta G°$/kcal mol^{-1}			
	Galena	PbO(c)	SO_2(g)	$PbSO_4$(c)
400	22.811	42.662	71.959	185.603
500	22.502	40.299	71.941	176.831
600	22.117	37.985	71.809	168.009
700	21.503	35.507	71.610	158.982
800	22.084	33.056	72.879	151.205
900	19.971	30.643	70.865	140.824

Table 3 Standard free energy (ΔG^o) and equilibrium constant (K) of the reaction of oxidized roasting of galena to the oxide

Temperature/°C	$-\Delta G°$/ kcal mol^{-1}	$-\Delta G°$/ kJ mol^{-1}	log$K$	K
400	183.620	768.450	59.6286	$4.25\cdot10^{59}$
500	179.476	751.107	50.7431	$5.53\cdot10^{50}$
600	175.354	733.857	43.8987	$7.92\cdot10^{43}$
700	171.228	716.589	38.4602	$2.89\cdot10^{38}$
800	167.102	699.322	34.0386	$1.09\cdot10^{34}$
900	163.076	682.473	30.3838	$2.42\cdot10^{30}$

$$\Delta G^\circ_{\text{reaction}} = 2\Delta G^\circ_{\text{PbO}} + 2\Delta G^\circ_{\text{SO}_2} - 2\Delta G^\circ_{\text{galena}} - 3\Delta G^\circ_{\text{O}_2}$$

$$= -2\cdot33.056 - 2\cdot72.579 + 2\cdot22.084 + 0.00 \quad (11)$$

$$= -167.102 \text{ kcal mol}^{-1}$$

$$\log K = \frac{167102}{4.57562\cdot1073} = 34.0386 \quad (12)$$

$$K = 1.09\cdot10^{34}$$

The standard free energy ($\Delta G°$) and equilibrium constant (K) for the reaction of oxidized roasting of galena to lead oxide were calculated at different temperatures and given in Table 3. It is observed that the equilibrium constant (K) is large and the reaction of oxidized roasting of galena to lead oxide is considered in practice to be an irreversible one. The oxidation of galena should preferably carried out at low concentration of oxygen in the gaseous phase. The rate of roasting of galena and its completeness depends on the rate of flow of air. The plot of the calculated standard free energy ($\Delta G°$) data *vs.* temperature (Fig. 2) shows the linear proportionality between them. The plot of log$K$ *vs.* $1/T$ (Fig. 3) yields a straight line, from which the calculated heat of the reaction ΔH at 700–800°C is 203.13 kcal mol^{-1} (850.1 kJ mol^{-1}). This value is in good agreement with the previously reported literature value of 201.7 kcal mol^{-1} [8, 17, 20]. The high exothermic heat released in the oxidation of galena satisfies the possibility of carrying out its oxidized roasting via the resulting heat.

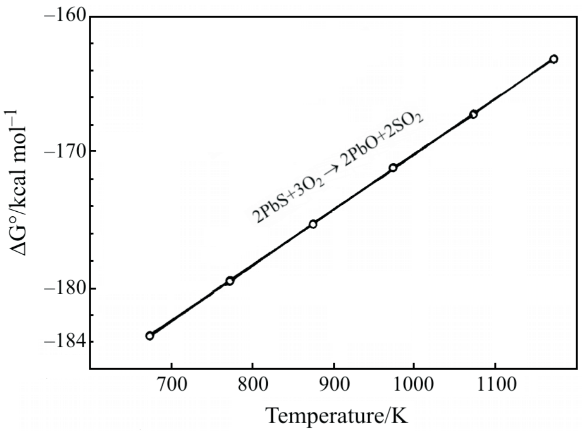

Fig. 2 Free energy diagram for oxidized roasting of galena

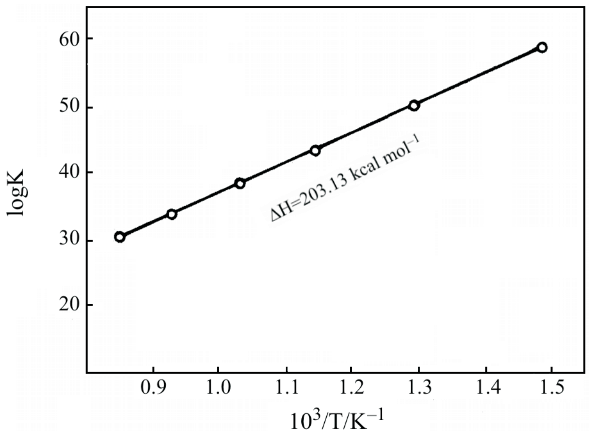

Fig. 3 Plot of log K *vs.* $10^3/T$ (K^{-1})

Results and discussion

DTA of roasting of fine grained galena

The thermal analysis data on the oxidized roasting of fine grained galena (particle size 0.06 mm) (Fig. 4) shows the beginning of its oxidation at 250°C and its conversion to lead sulphate (anglesite). The wide and small exothermic peak at 460°C represents the intensive formation of lead sulphate. This is followed by another small exothermic peak at 580°C, representing the reaction between galena and the lead sulphate resulted with the formation of basic lead sulphate ($PbSO_4\cdot PbO$). The intensive oxidation of galena is represented by the large and sharp exothermic triple maximum peak, at 730, 740 and 765°C, accompanied by an increase in mass (TG). This mass increase is due to the formation of lead sulphate and different basic sulphates. These sulphates are anglesite at 300°C, $PbSO_4\cdot PbO$ at 600°C, $PbSO_4\cdot 2PbO$ at 800°C and $PbSO_4\cdot 4PbO$ at 900°C. as identified by XRD. The gain in mass of solid sulphate product is more than the escape of SO_2. Most of sulphur dioxide resulted is

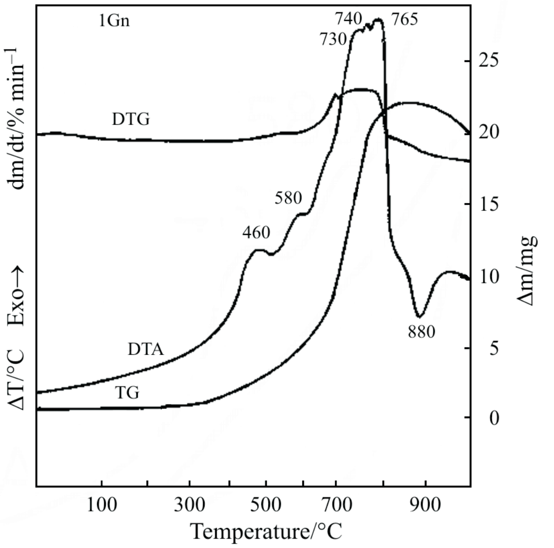

Fig. 4 TG, DTG and DTA curves of oxidized roasting of fine grained galena (0.06 mm). Mass of sample 187 mg; heating rate 10°C min^{-1}

consumed in the formation of sulphates. The mass loss is observed at higher temperature than 900°C due to the dissociation of the sulphates and basic sulphates to lead oxide and evolution of SO_2. The medium endothermic peak at 880°C reflects the melting and vaporization of lead oxide and also the reaction between galena and lead oxide and sulphate with the formation of lead.

The results obtained are consistent with literature data [1–3, 6, 8, 9, 11, 17, 20–23, 25] as the oxidation of galena and its conversion to lead sulphate remarkably takes place at 200–300°C but slowly. Lead sulphate is mainly formed on oxidized roasting of galena at temperature lower than 450–500°C. Lead sulphate is unstable at high temperature and begins its dissociation at 637°C and its intensive dissociation takes place at 705°C with the formation of basic lead sulphates. These lead sulphates intensively decomposed at temperature higher than 950°C to lead oxide.

It is observed that at lower temperature than 600°C, the mineral is quite inert, undergoing only low oxidation until the ignition temperature is reached. Beyond this limit, the rate of oxidation of galena is high and the reaction takes place spontaneously with the heat released. Galena has a comparatively high ignition temperature with respect to the other sulphide minerals (755°C for fine galena particles with a particle size 0.075 mm) [1, 8, 11]. The DTA curve of galena shows several exothermic peaks at 770°C and wide large exothermic peak with maximum at 854, 874, 885 and 910°C. The reaction between lead sulphide and sulphate begins at 550°C with the formation of lead oxide or lead under definite conditions and at 725°C the pressure of sulphur dioxide equals 1 atm. The reaction between galena and lead oxide begins at 650–660°C and intensively takes place at 700°C as endothermic one with the formation of lead. The vapour pressure of sulphur dioxide at 800 and 870°C equals 90 and 830 mm Hg, respectively. The reactin between galena and lead sulphate takes place effectively at 700–750°C (the vapour pressure of sulphur dioxide at 750°C is 730 mm Hg). The lead formed oxidizes in air atmosphere to lead oxide, which is also resulted from the reaction of lead with lead sulphate.

Microscopic and X-ray diffraction study

The products of the runs at 300, 600, 800, 900 and 1000°C within 30 min were identified microscopically and by using X-ray diffraction.

At 300–500°C, galena and anglesite constitute the total composition of polished and thin sections. Galena particles are covered by a thick compact layer of anglesite. This layer prevents the diffusion of air and the oxidation of galena is low. All particles are partially desulphurized and sulphatized. In polished sections, the particles show a homogeneous white core composed of galena, surrounded by a dark layer of anglesite. At 800°C, the surface sulphate layer around galena grains is a friable one and porous. The core of the particles is altered and the surface coating of the particles is cracked due to the high rate of the reaction of oxidation of galena at 800°C, accompanied by some fragmentation of the particles. At 900 and 1000°C, galena is not observed in the polished sections of such products, indicating its complete desulphurization and oxidation.

The X-ray diffraction patterns of these products are shown in Fig. 5 (a, b, c, d and e at 300, 600, 800, 900 and 1000°C, respectively). At 300°C, the product of roasting of galena is composed of galena and anglesite. This indicates low oxidation of galena and its sulphatization with the formation of anglesite, due to the reaction of sulphur dioxide with lead oxide formed. At 600°C, the phase of this product is basic lead sulphate of composition $PbSO_4{\cdot}PbO$ with some anglesite and small amount of lead oxide. The basic lead sulphate is formed at the expense of anglesite and by the reaction between galena and anglesite or anglesite with lead oxide. At 800°C, the phase $PbSO_4{\cdot}2PbO$ is seen to be the main constituent of the product with basic lead sulphate $PbSO_4{\cdot}PbO$, lead oxide and small amount of anglesite. The formation of the phase $PbSO_4{\cdot}2PbO$ may be due to the reaction between galena and $PbSO_4{\cdot}PbO$ or lead sulphate with the lead oxide [1, 8, 20, 23]. At 900°C, the product of roasting is composed mainly of the phase $PbSO_4{\cdot}4PbO$ and lead oxide with small amount of the

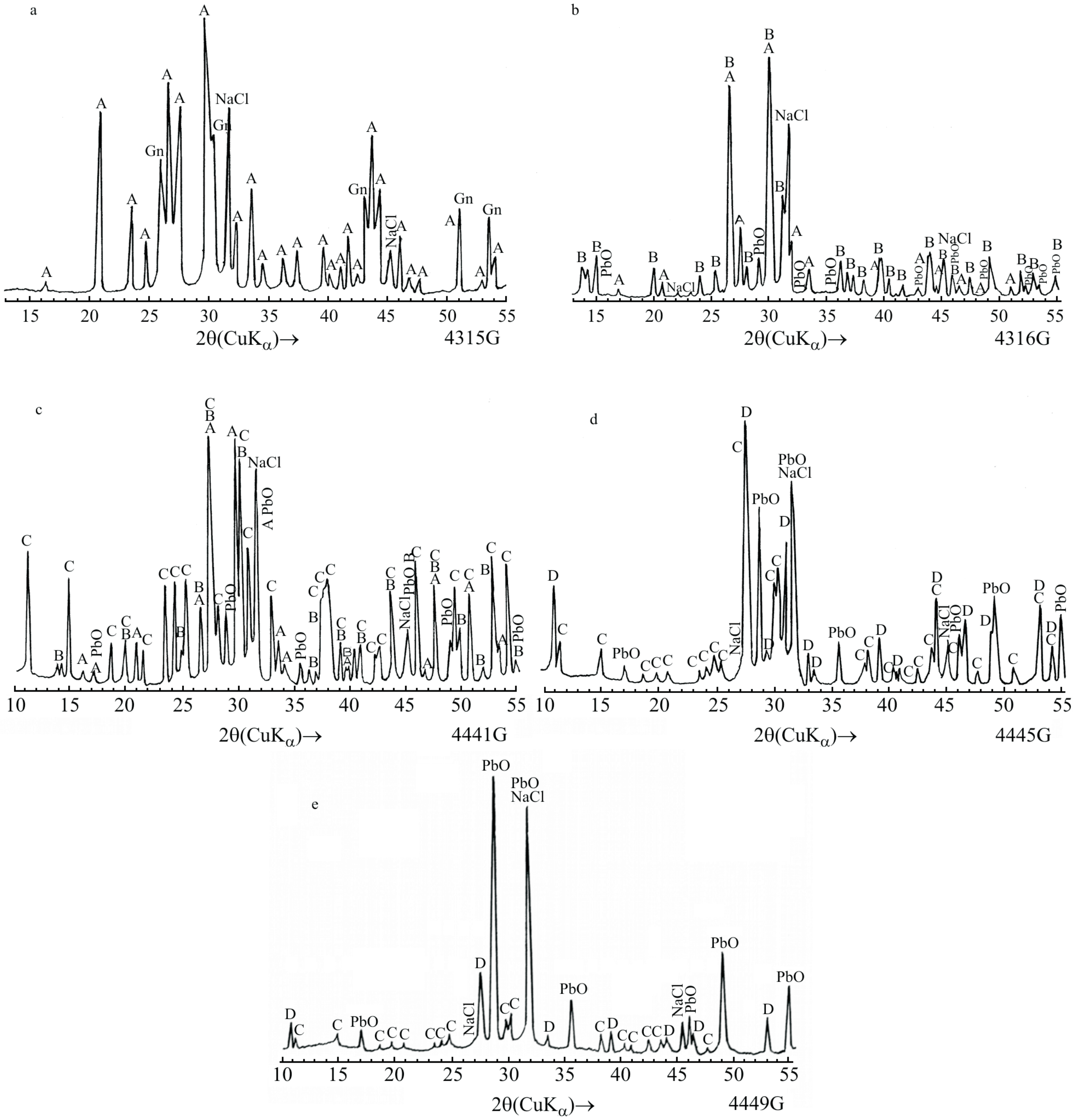

Fig. 5 X-ray diffraction patterns of the products of oxidized roasting of galena. (a, b, c, d and e at 300, 600, 800, 900 and 1000°C, repectively); *Gn* = galena, *A*= anglesite, *B*= $PbSO_4{\cdot}PbO$, *C*= $PbSO_4{\cdot}2PbO$, *D*= $PbSO_4{\cdot}4PbO$ and *PbO*= lead oxide

phase $PbSO_4{\cdot}2PbO$ and the disappearance of the phase $PbSO_4{\cdot}PbO$. The composition of this product at such temperature reflects the quite desulphurization and oxidation of galena to lead oxide.

At 1000°C, lead oxide constitutes the total composition of the end product of roasting with small amount of $PbSO_4{\cdot}4PbO$ and traces of the phase $PbSO_4{\cdot}2PbO$. This reflects the high oxidation and desulphurization of galena at 1000°C. This indicates why the second stage of oxidized roasting of galena in industry is performed at 1000–1100°C to attain complete oxidation, desulphurization of the product and the decomposition of all lead sulphate and basic sulphates, which are formed as intermediate products. Consequently, lead oxide is produced as the end product of roasting. The X-ray peaks of lead oxide (Fig. 5e) are well defined, sharp and intense suggesting good crystallinity.

Lead was not detected in the products of roasting of galena, as indicated by the absence of its peaks in all X-ray diffraction patterns.

The X-ray diffraction study of the products of oxidized roasting of galena at different temperatures is consistent with literature data [1, 8, 11, 20, 23], as oxidation of lead sulphide proceeds via lead sulphate and basic lead sulphates before being oxidized to lead oxide. Lead sulphide is converted to lead sulphate at low temperature (200–300°C) and to basic lead sulphate at 400–600°C at the expense of lead sulphate, at 800–900°C to $PbSO_4{\cdot}2PbO$ and at 900–950°C to $PbSO_4{\cdot}4PbO$ before being completely desulphurized to lead oxide.

DTA of roasting of coarse graind galena

The thermal analysis data on the oxidized roasting of coarse grained galena (particle size 0.125 mm) (Fig. 6) reveal similar peaks at slightly higher temperature than for the fine grained galena sample with a particle size of 0.06 mm. Here the intensive oxidation of galena is reflected by the large and sharp exothermic double maximum peak at 750 and 780°C. This effect is accompanied by a gain of mass (TG curve), due to the formation of lead sulphate and basic sulphate with lead oxide. The reaction of unreacted galena with lead oxide and sulphate and the melting of lead oxide resulted are represented by the wide and small endothermic peak at 883°C. At temperature higher than 900°C, lead sulphate and basic sulphate decomposed as shown by the loss in mass (TG) and intensively dissociated at 1000°C.

The thermal analysis study of oxidized roasting of galena shows that different products are obtained, depending on the temperature of roasting. The mechanism of the reaction is a complicated one and can be considered as the following :

At 200–450°C: The oxidized roasting of galena takes place with the formation of lead sulphate according to the following reactions:

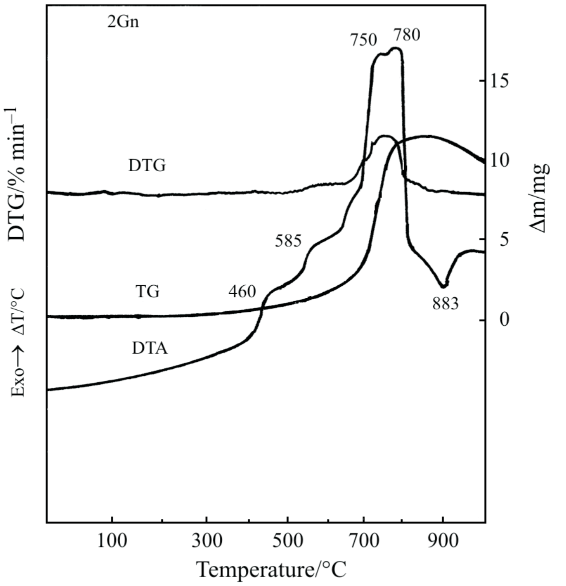

Fig. 6 TG, DTG and DTA curves of oxidized roasting of coarse grained galena (0.125 mm). Mass of sample 200 mg; heating rate 10°C min^{-1}

$$2PbS+3O_2 \rightarrow 2PbO+2SO_2 \qquad (13)$$

$$2PbO+2SO_2+O_2 \rightarrow 2PbSO_4 \qquad (14)$$

or the reactions of oxidation of galena may take place according to slow or fast roasting as:

$$2PbS+3.5O_2 \rightarrow PbO+PbSO_4+SO_2 \qquad (15)$$

$$3PbS+5O_2 \rightarrow 2PbO+PbSO_4+2SO_2 \qquad (16)$$

This leads to partial oxidation of galena and the products are lead sulphate and oxide.

At 500–700°C: Galena reacts with lead sulphate or with lead oxide with the formation of $PbSO_4{\cdot}PbO$ and lead oxide, according to the following reactions:

$$PbS+7PbSO_4 \rightarrow 4(PbSO_4{\cdot}PbO)+4SO_4 \qquad (17)$$

$$PbSO_4+PbO \rightarrow PbSO_4{\cdot}PbO \qquad (18)$$

$$PbS+3PbSO_4 \xrightarrow{550^{\circ}C} 4PbO+4SO_2 \qquad (19)$$

Also, lead sulphide may react with lead oxide or sulphate at 650–700°C with the formation of lead according to:

$$PbS+2PbO \rightarrow 2Pb+SO_2 \qquad (20)$$

$$PbS+PbSO_4 \rightarrow 2Pb+2SO_2 \qquad (21)$$

The lead resulted may oxidize in air atmosphere or reacts with lead sulphate with the formation of lead oxide according to:

$$2Pb+O_2 \rightarrow 2PbO \qquad (22)$$

$$Pb+PbSO_4 \rightarrow 2PbO+SO_2 \qquad (23)$$

At 800°C: The lead sulphide may react with lead basic sulphate or lead sulphate with lead oxide with the formation of $PbSO_4{\cdot}2PbO$, according to:

$$PbS+10(PbSO_4{\cdot}PbO) \rightarrow 7(PbSO_4{\cdot}2PbO)+4SO_2 \qquad (24)$$

or

$$PbSO_4+2PbO \rightarrow PbSO_4{\cdot}2PbO \qquad (25)$$

At 900°C: The formation of $PbSO_4{\cdot}4PbO$ may proceed in different ways. One starts from galena oxidation or its reaction with $PbSO_4{\cdot}2PbO$, according to :

$$5PbS+8O_2 \rightarrow PbSO_4{\cdot}4PbO+SO_2 \qquad (26)$$

$$2PbS+2PbO+3O_2 \rightarrow PbSO_4{\cdot}4PbO+2SO_2 \qquad (27)$$

The second from the reaction between $PbSO_4{\cdot}2PbO$ and lead oxide, according to:

$$PbSO_4{\cdot}2PbO+2PbO \rightarrow PbSO_4{\cdot}4\,PbO \qquad (28)$$

At 950–1000°C: Lead oxide is the end product of oxidized roasting of galena. It is formed as the product of oxidation of galena and the dissociation of intermediate oxidation products such as $PbSO_4$,

$PbSO_4 \cdot 2PbO$ and $PbSO_4 \cdot 4PbO$ which are unstable at high temperature according to the following:

$$2PbS+3O_2 \rightarrow 2PbO+2SO_2 \quad (29)$$

$$PbSO_4 \rightarrow PbO+SO_3 \quad (30)$$

$$PbSO_4 \cdot 2PbO \rightarrow 3PbO+SO_3 \quad (31)$$

$$PbSO_4 \cdot 4PbO \rightarrow 5PbO+SO_3 \quad (32)$$

General characteristics of the lead oxide produced

The crystals of lead oxide are transparent, coloured dark red and have greasy lustre. In thin sections, it is coloured red, crystallizes in the tetragonal system in the form of tabular crystals with perfect (110) cleavage and is optically negative.

The X-ray diffraction pattern of the product of the run at 1000°C (Fig. 5E) shows that lead oxide constitutes the total composition of the end product of roasting with small amount of $PbSO_4 \cdot 4PbO$ and traces of $PbSO_4 \cdot 2PbO$. The galena and anglesite peaks are completely disappeared, indicating completeness of oxidation of galena and the dissociation of lead sulphate and basic sulphates to lead oxide. The X-ray peaks of lead oxide are well defined, sharp and intense, suggesting good crystallinity. The X-ray diffraction data on the lead oxide produced are consistent with the corresponding values for the standard lead oxide (Table 4).

The unit cell dimensions and constants of the lead oxide produced are given in Table 5. It is observed that the calculated cell dimensions, constants and optic axial angles of the lead oxide produced are consistent with the corresponding data for the standard one.

Table 4 X-ray powder diffraction data on lead oxide

d/Å		I/I_0/%		*h k l*
ASTM	Observed	ASTM	Observed	
5.018	5.0177	5	7	0 0 1
3.115	3.1153	100	100	1 0 1
2.809	2.8132	62	65	1 1 0
2.510	2.5110	18	21	0 0 2
2.124	2.1247	1	1	1 0 2
1.988	1.9930	8	9	2 0 0
1.872	1.8685	37	37	1 1 2
1.675	1.6687	24	26	2 1 1
1.558	1.5590	6	5	2 0 2
1.542	1.5440	11	10	1 0 3
1.438	1.4390	2	3	1 1 3
1.405	1.4070	5	5	2 2 0
1.282	1.2840	2	2	3 0 1, 2 0 3
1.256	1.2573	3	4	3 1 0
1.226	1.2265	4	4	2 2 2
1.219	1.2188	5	5	3 1 1, 3 1 2
1.1977	1.1976	<1	1	1 0 4
1.1462	1.1458	2	2	1 1 4
1.1232	1.1233	2	2	3 1 2
1.0768	1.1077	3	3	3 2 1, 2 2 3
1.0610	1.1061	2	2	2 0 4

Table 5 Unit cell dimensions and axial angles of lead oxide produced

Material	*a*/Å	*c*/Å	α_{deg}	β_{deg}	γ_{deg}	V/Å^3
Lead oxide	3.9662	5.0184	90.00	90.00	90.00	78.943
	±0.0105	±0.0207	00.00	00.00	00.00	±0.014
Standard	3.9820	5.011	90.00	90.00	90.00	79.456

Conclusions

This thermal analysis study of the oxidized roasting of galena has demonstrated that the beginning of its oxidation leads to the formation of lead sulphate (anglesite) as represented by the wide and small exothermic peak at 460°C. This is followed by another small exothermic peak at 580°C, representing the formation of basic lead sulphate ($PbSO_4 \cdot PbO$) at the expense of lead sulphate by the reaction between galena and anglesite. The intensive oxidation of galena is represented by the large and sharp exothermic triple maximum at 730, 740 and 765°C with the formation of basic lead sulphates and some lead oxide. This is accompanied by a large gain in mass (TG), due to the formation of lead sulphate and basic sulphate. Most of sulphur dioxide resulted from the oxidation of galena is consumed in the formation of lead sulphate and basic sulphates due to its reaction with lead oxide. The medium endothermic peak at 880°C reflects the melting and vaporization of lead oxide resulted and also the reaction between galena and lead oxide and sulphate with the formation of basic lead sulphates.

The standard free energy ($\Delta G°$) and equilibrium constant (K) of the reactions of oxidation of galena to lead oxide at 800°C are –167.102 kcal mol^{-1} (699.322 kJ mol^{-1}) and $1.09 \cdot 10^{34}$ and to the lead oxide and sulphate –212.67 kcal mol^{-1} (890.024 kJ mol^{-1}) and $2.1 \cdot 10^{43}$, respectively. These values reflect the irreversibility of the reactions.

The products of the oxidized roasting of galena are different, depending upon the temperature of its roasting such as lead sulphate (anglesite) at 300°C, basic lead sulphates of specified compositions: $PbSO_4 \cdot PbO$ at 600°C, $PbSO_4 \cdot 2PbO$ at 800°C and $PbSO_4 \cdot 4PbO$ at 900°C and lead oxide at 1000°C. Lead oxide constitutes the total composition of the end product of roasting of galena at 1000°C with small amount of $PbSO_4 \cdot 4PbO$ and traces $PbSO_4 \cdot 2PbO$.

The oxidized roasting of galena results in the production of lead oxide, which is considered as the starting material of lead industry. The lead oxide produced is crystalline and its crystals are transparent, colored dark red and have greasy luster. In thin sections, it is red, crystallizes in the tetragonal system in the form of tabular crystals with perfect (110) cleavage and is optically negative.

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Received: October 4, 2005
Accepted: June 7, 2006

DOI: 10.1007/s10973-005-6785-6