Thermodynamic analysis of the direct converting of lead sulphide

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SYNOPSIS

High-temperature phase relations and thermodynamics of the condensed phase region of the Pb-S-O system at 1473 K were analysed by use of the available information. The sub-regular solution models on Pb-PbS and PbO-PbSO$_4$ continuous melts were used in conjunction to generate a consistent set of thermodynamic and phase-equilibrium conditions for the Pb-S-O system. The directions and distributions of conjugation lines between melts of this system were derived with relevant activity and composition data. The calculations permited the thermodynamic analysis of direct lead smelting and the construction of isothermal reaction diagrams for the system in terms of oxygen and sulphur partial pressures at 1473 K.

SAMEVATTING

Die hoëtemperatuurfaseverhoudings en -termodinamika van die gekondenseerdefasegebied van die Pb-S-O-stelsel by 1473 K is met gebruik van die beskikbare inligting ondersoek. Die subreëlmatige oplossingmodelle vir kontinue smeltings van Pb-PbS en PbO-PbSO$_4$ is saam gebruik om 'n konsekwente stel termodinamiese en fase-ewewigstoestande vir die Pb-S-O-stelsel te genereer. Die rigting en verdeling van konjugasielyne tussen smeltings van hierdie stelsel is afgelei met behulp van die toepaslike aktiwiteits- en samestellingsdata. Die berekenings het die termodinamiese ontleding van regstreekse loodsmelting en die konstruksie van isotermiese reaksiediagramme vir die stelsel in terme van suurstof- en swaeldeeldrukke by 1473 K moontlik gemaak.

Background

The lead blast furnace, together with a sintering machine, has been the main production unit of the lead-smelting industry for over half a century. It accounts for approximately 80 per cent of the world's production of lead bullion.

Despite many technological improvements, blast-furnace smelting has several important disadvantages, the overall thermal inefficiency of the two-step operation being its main drawback. The lead content of lead concentrates from modern ore-dressing plants ranges from 65 to 80 per cent. For blast-furnace smelting, the concentrates must be desulphurized and agglomerated by sintering. A requirement for the perfect operation of a down-draft sintering machine and of a blast furnace is that the maximum lead content in the feed must be 40 to 45 per cent. For this reason, lead concentrates must be diluted by the addition of return slags, limestone, and possibly iron oxide and silica. For example, 100 t of lead concentrate containing 70 per cent lead would contain about 19 t of gangue. To produce a perfect sinter with 42 per cent lead, it would be necessary to add about 67 t of flux and return slag (more than three times the original mass of the gangue) to the sinter mix and blast-furnace charge. About 20 t of coke would be necessary to smelt this charge in the blast furnace. Meanwhile, the sulphur content of the concentrate, about 11 t, which would otherwise serve both as a reducing agent and as a fuel, has to be eliminated during the sintering operation.

The first step towards an intelligent use of sulphur in sulphide lead concentrates has been the revival of the ancient Newnam ore-hearth process during the past thirty years. The modern hearth processes, under trade names like Bolidens, Lurgi, and BBU (Bleiberger Bergwerks Union, Austria), take advantage of the following roasting reactions:

$$PbS + 2 PbO = 3 Pb + SO_2 \quad\dots\dots\dots\dots\dots (1)$$

$$PbS + PbSO_4 = 2 Pb + 2 SO_2, \quad\dots\dots\dots\dots (2)$$
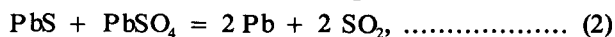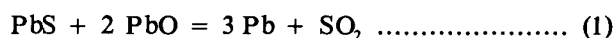
where PbS is the starting material, and PbO and PbSO$_4$ are formed through controlled oxidation of PbS with air. Reactions leading to the formation of PbO and PbSO$_4$ and those in (1) and (2) are strongly exothermic. Therefore, theoretically, the production of lead by the ore-hearth process can proceed autogenously.

The principles of the ore-hearth process are described schematically on the Pb-S-O composition triangle depicted in Fig. 1. When oxygen is added to PbS, the composition of the product moves towards the oxygen apex of the Pb-S-O ternary, and the compound PbSO$_4$ forms. At process temperatures, 700 to 1100°C, PbSO$_4$ decomposes into basic sulphates. Consequently, products are formed as indicated on the line PbO-PbSO$_4$. Part of the initial PbS remains unchanged since, intentionally, the oxidation is not carried out to completion. Thus, the reaction mixture has composition like A and B in Fig. 1; the metallic lead in these mixtures is formed according to the simplified roasting reactions (1) and (2).

The production of lead with modern versions of the ore-hearth process is intermittent in nature. The product lead may contain either an excess of sulphur or an excess of oxygen depending upon the supply of oxygen to the system. Hence, the bullion must be processed further to

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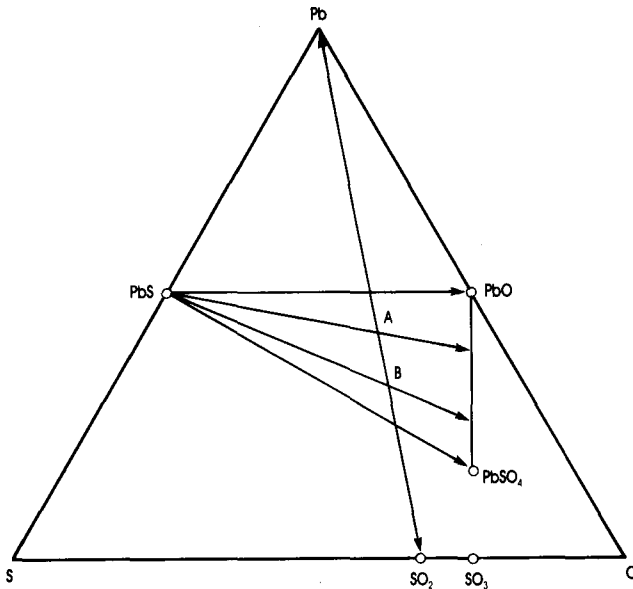
Fig. 1—Roasting reactions in the system Pb–S–O

upgrade the lead to a marketable quality. Furthermore, the specific production capacity is much lower compared with blast-furnace smelting because longer retention times are necessary for the separation of liquid lead from the reacting mass and its subsequent settling into the lead hearth.

The most recent trend in lead production is direct smelting of sulphide concentrates in a single step. The direct-smelting, otherwise known as continuous-smelting, process for lead takes advantage of the overall reaction

$$PbS + O_2 = Pb + SO_2, \quad \text{............................} \quad (3)$$
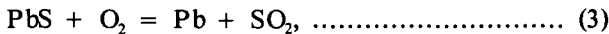
in which PbS occurs as a liquid phase at the temperature of the process (about 1200°C). Local over-oxidation causes the following reactions to occur:

$$PbS + 2 O_2 = PbSO_4 \quad \text{..............................} \quad (4)$$

$$PbS + 3/2 O_2 = PbO + SO_2. \quad \text{....................} \quad (5)$$
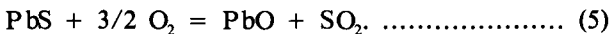
At 1200°C, PbO and PbSO$_4$ collect in the slag phase but, given sufficient time, they are reduced by sulphur in the bullion according to

$$PbSO_4 + S = Pb + 2 SO_2 \quad \text{.........................} \quad (6)$$

$$2 PbO + S = 2 Pb + SO_2. \quad \text{.........................} \quad (7)$$
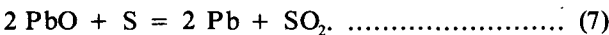
Reactions (6) and (7) are commonly referred to as slag-cleaning reactions and are essentially similar in nature to reactions (1) and (2). Hence, in a way, the continuous-smelting process resembles the ore-hearth process except that the reactions occur between liquid phases, which results in a higher production rate.

Although reactions (3) to (7) are commonly used to describe the chemistry of the process, there is a considerable lack of basic information on the thermodynamics and phase equilibria involved between the various liquid phases formed in the ternary Pb–S–O system. Obviously, an understanding of the equilibrium relations among metal, slag, and gas phases is essential for the successful operation and design of any smelting process. The information available in the literature on systems pertinent to the present study is reviewed in this paper.

Review of the Literature

The System Pb–PbS

The Pb–PbS system is a part of the main Pb–S binary. The phase diagrams published in the past for this system gave rise to controversy. There were those[1–3] with a single eutectic reaction around 326°C and having a continuous liquidus curve extending from the eutectic point up to the melting point of PbS. The second group of phase diagrams included a monotectic reaction at approximately 1040°C in addition to the low-temperature eutectic, resulting in liquid immiscibility[4,5]. However, the recent work of Eric and Timucin[6] has proved the non-existence of liquid immiscibility. They have redrawn the high-temperature portion of the PbS liquidus derived from their sub-regular solution model. The sub-regular solution model fitted very well to their experimental PbS activities obtained by an iso-piestic technique. The derived liquidus from the model was also in excellent agreement with their experimental findings. Their results are used in this investigation, and the following summarize their important equations:

$$\ln a_{PbS} = \ln(n_S/n_{Pb}) + 1/T\,[2006 + 891\,(n_s/n_{Pb})]$$

$$\left[\frac{n_{Pb} - n_S}{n_{Pb}}\right]^2, \quad \text{..} \quad (8)$$

$$\ln a_{Pb} = \ln\frac{n_{Pb} - n_S}{n_{Pb}} + 1/T$$

$$\left[2453 - 891\left(\frac{n_{Pb} - n_S}{n_{Pb}}\right)\right]\left[\frac{n_S}{n_{Pb}}\right]^2, \quad \text{.....} \quad (9)$$

$$T = \frac{\left[\dfrac{n_{Pb} - n_S}{n_{Pb}}\right]^2 [2006 + 891\,(n_S/n_{Pb})] + 5942}{4{,}287 - \ln\,(n_S/n_{Pb})}, \quad (10)$$

where n_{Pb} and n_S are the number of moles of lead and sulphur respectively. The term n_S/n_{Pb} corresponds to the mole fraction of PbS, and $(n_{Pb} - n_S)/n_{Pb}$ corresponds to the mole fraction of Pb. Equation (10) gives the high-temperature position of the PbS liquidus curve. For more complete information on the phase equilibria and thermodynamics of the Pb–PbS system, the reader is referred to the work of Eric and Timucin[6].

The System Pb–PbO

A phase diagram for the system Pb–PbO was compiled by Shunk[7], which is reproduced in Fig. 2. The system has a eutectic isotherm at 326°C, and the transformation at 540°C designates the transition of PbO from tetragonal (red) to orthorhombic (yellow) modification. A wide miscibility gap originating at the monotectic isotherm (850°C) and extending to high temperatures is a characteristic of this system. The metallic and oxide melts are sparingly soluble in each other.

For the formation of liquid PbO from liquid Pb and gaseous oxygen, according to the reaction

$$Pb(l) + \frac{1}{2} O_2(g) = PbO(l), \quad \text{.....................} \quad (11)$$
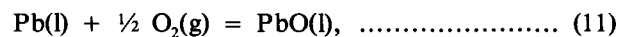
the data compiled by Kellogg[8] can be used to derive the following linear temperature dependence of the standard free-energy change:
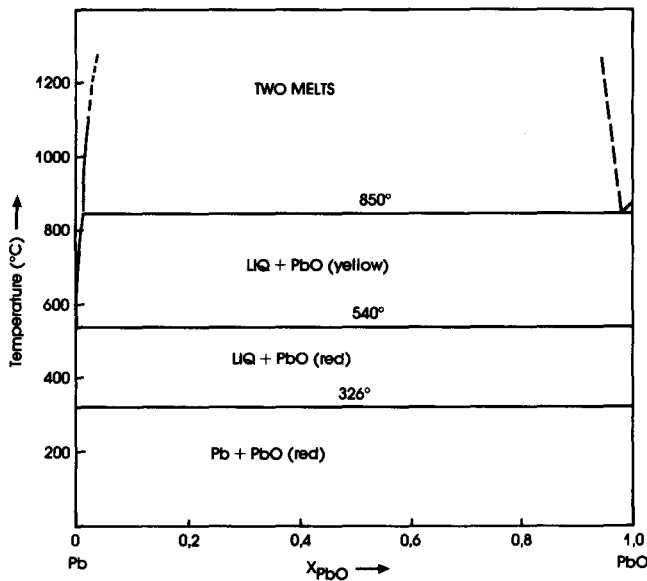
Fig. 2—Phase diagram for the system Pb–PbO (after Shunk[7])

$$\Delta G^\circ = -183\,004 + 69,19\,T \text{ J/mole.} \qquad (12)$$

Equation (12) is valid in the temperature range 1200 to 1500 K.

The System Pb–S–O

The solid-state thermodynamic properties of the system Pb–S–O were studied in considerable detail by Kellogg and Basu[9] at temperatures up to 827°C. The data produced in a later work, that of Tuffley and Russell[10], is only supplementary in nature, and produced a hypothetical roasting equilibrium diagram at 1200°C. This diagram and a similar one constructed by Yazawa and Gubcova[11] at 1100°C are wrong in principle because, in their thermodynamic calculations, they regarded various oxy-sulphates that are molten at these temperatures as solid compounds. Schuhmann *et al.*[3] calculated activities of PbO in the Pb–S–O system from their regular treatment of Pb–S liquids by the reaction between PbS, Pb, PbO, and SO_2 at 1 atm pressure, neglecting the presence of $PbSO_4$. Therefore, their picture is not complete.

A three-dimensional model illustrating the equilibrium assemblages between various condensed phases of the Pb–S–O system[12] as constructed from the data of Kellogg and Basu[9] is shown in Fig. 3. The compatibility relations at sub-solidus temperatures apply to the roasting of lead sulphide; the noteworthy feature of such relations is the appearance and disappearance of various oxy-sulphates as a function of temperature.

At temperatures above liquid formation, two distinct series of liquid solutions develop in the system. These are Pb–PbS continuous liquids[6,12] and PbO–PbSO$_4$ liquids[9]; the former corresponds to the metal phase, and the latter is the slag phase of the continuous lead-smelting processes (excluding gangue and flux). Thus, an understanding of thermodynamic fundamentals of the process should evolve from a knowledge of the equilibria in the Pb–PbS–PbSO$_4$–PbO sub-system of the mother Pb–S–O ternary. Clearly, this knowledge could be obtained from the directions of conjugation lines between the co-existing metal and slag phases, upon which no information is
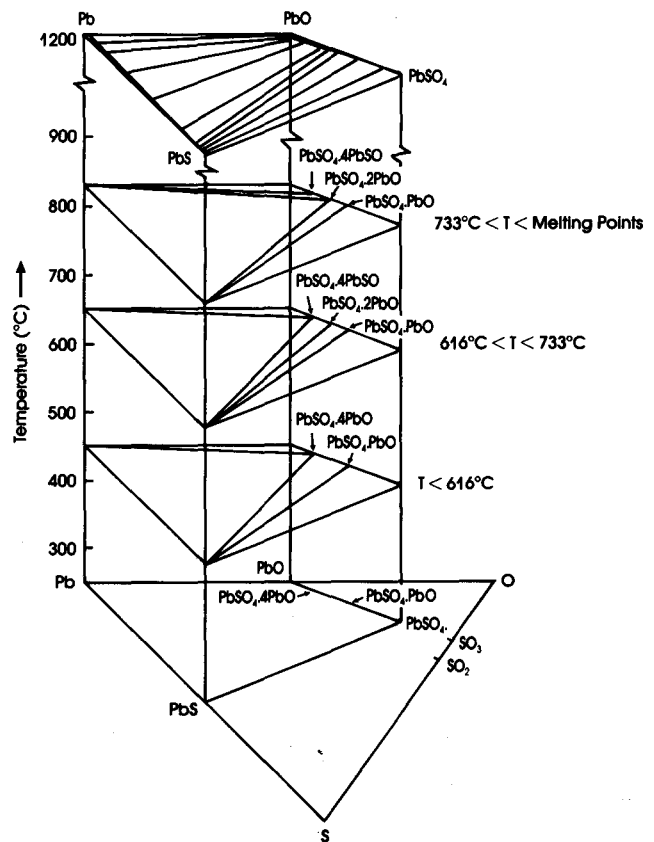

Fig. 3—Three-dimensional model illustrating the equilibrium assemblages between various condensed phases of the system Pb–S–O (the compatibility relations at temperatures below liquid formation being after Kellogg and Basu[9])

available. The conjugation lines shown on the topmost trapezoid of Fig. 3 are hypothetical and only illustrative.

The modified phase diagram[9] for the binary system PbO–PbSO$_4$ is reproduced in Fig. 4. At the smelting temperatures (about 1200°C), the two end members mix in all proportions in the liquid state and, whereas various oxy-sulphates decompose or melt at temperatures lower than 1000°C, PbSO$_4$ remains solid up to 1170°C.

The activities of PbO in PbO–PbSO$_4$ melts were measured by Jacob and Toguri[13] using electromotive-force and gas-equilibration techniques. The increased rate of volatilization of PbO at temperatures above 1000°C and problems arising from crucible interference confined their measurements to a maximum temperature of 980°C. The activities of both components deviated negatively from ideality, and they fitted the activity data to a sub-regular solution model. They obtained the following equations for the activity coefficients of PbO and PbSO$_4$:

$$RT \ln\gamma_{PbO} = X^2_{PbSO_4} (-42\,450 + 20\,000\,X_{PbSO_4}) \text{ J/mole} \qquad (13)$$

$$RT \ln\gamma_{PbSO_4} = X^2_{PbO} (-12\,450 - 20\,000\,X_{PbO}) \text{ J/mole.} \qquad (14)$$

The PbS–PbSO$_4$ join of the system has not been studied experimentally, and there is no information available on this system. However, it is known that PbS and PbSO$_4$ react to form liquid Pb and SO_2 gas as shown in reaction (2). A major problem encountered by investi-

1200

1100

1000

900

800

700

600

500

Temperature (°C)

LIQUID

1170°→

961°   975°

950°

960°

886°

895°

835°

PbSO₄.2PbO

PbSO₄.PbO

PbSO₄.4PbO →

616°

0   0,2   0,4   0,6   0,8   1,0

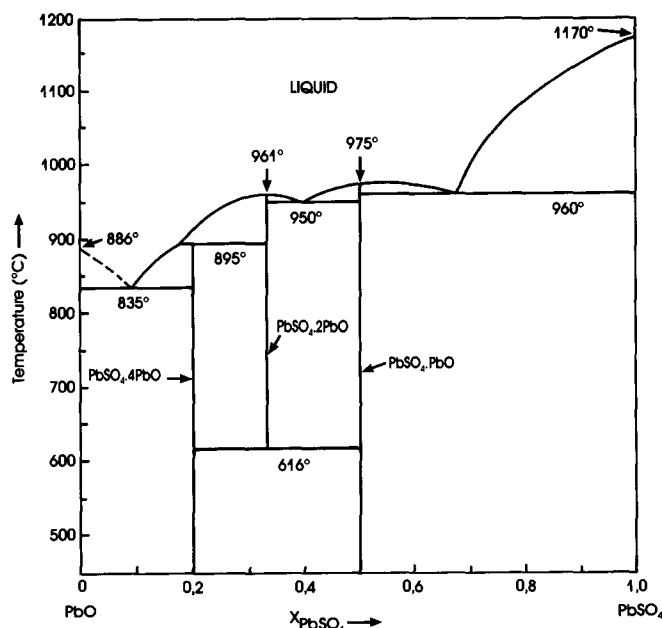PbO X_{PbSO_4} →   PbSO₄

Fig. 4—Phase diagram for the system PbO-PbSO₄, (after Kellogg and Basu[9])

gators is to find a suitable crucible that is inert both to oxygen and sulphur, which are present in appreciable amounts in the PbS-PbSO₄ system, and strong enough to withstand the high SO₂ pressures generated. The experiments conducted by Eric[12] were unsuccessful owing to the explosion of evacuated and sealed silica capsules containing the PbS-PbSO₄ mixtures, which were contained in alumina crucibles introduced into the silica capsules. For the purposes of this work, it can be assumed, in the absence of data, that PbS and PbSO₄ are immiscible in the liquid state.

Thermodynamics in the Converting of Lead Sulphide

Reaction (3) can be regarded as the overall reaction in the converting of lead sulphide to metal, and involves a system of three components; Pb, S, and O. Lead bullion formed by reaction (3) contains sulphur in solution, and is in equilibrium with a slag containing PbO and PbSO₄, the level of which depends on the slag composition and on the oxygen partial pressure of the gas, as well as on temperature. For a practical and rapid converting process, SO₂ evolves spontaneously at about atmospheric pressure. As mentioned earlier, local over-oxidation can occur by reactions (9) and (5). At a smelting temperature of about 1200°C, PbO and PbSO₄ that have been collected in the slag phase can be reduced by sulphur in the bullion according to reactions (6) and (7) if sufficient time is given.

Modern direct lead-smelting processes are, in fact, an intensification of the old ore-hearth method, in so far as reactions (3) to (7) proceed simultaneously at high temperature in a single vessel. The thermodynamic control of lead converting involves the close control of the chemistry of the Pb-PbS liquid bath in equilibrium with the PbO-PbSO₄ slag melt as affected by oxygen and sulphur potentials at the smelting temperature. The results of Eric and Timucin[6] for Pb-PbS liquid solutions, together with the data provided by Jacob and Toguri[13] for PbO-

PbSO₄ melts, clearly bring out the overall conditions for the direct smelting of lead concentrates.

The following thermodynamic analysis makes use of the analytical expressions derived from sub-regular model treatment of both Pb-PbS[6] and PbO-PbSO₄[13] melts. In this manner, the equilibrium compositions of the slag and metal bath were evaluated from relevant thermodynamic information. Prior to the calculations, two assumptions had to be made. The Pb-PbO system, as stated previously, is characterized by a very large liquid miscibility gap at temperatures above 850°C. The first assumption was to extend this two-liquid region up to the PbSO₄-PbS join, with the liquidus lines within the ternary field coinciding with the binary PbO-PbSO₄ and Pb-PbS sections. The PbSO₄-PbS join is thus treated as having a liquid miscibility gap. The second assumption was to neglect the very small mutual solubilities at both ends of the Pb-PbO system. Therefore, it is possible to write two Gibbs-Duhem equations for the two liquid solutions in equilibrium with each other. For constant temperature and pressure, the equations are as follows:

$$X_{PbO} d \ln a_{PbO} + X_{PbSO_4} d \ln a_{PbSO_4} = 0 \quad\quad (15)$$

$$X_{Pb} d \ln a_{Pb} + X_{PbS} d \ln a_{PbS} = 0. \quad\quad (16)$$

For the reaction involving all these species,

$$4 \text{ PbO(l)} + \text{PbS(l)} = \text{PbSO}_4\text{(l)} + 4 \text{ Pb(l)}, \quad\ldots (17)$$
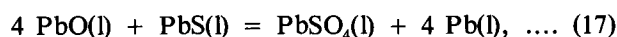
the equilibrium constant is

$$\ln K = \ln a_{PbSO_4} + 4 \ln a_{Pb} - \ln a_{PbS} - 4 \ln a_{PbO}. \quad (18)$$

Differentiation of equation (18) yields

$$d \ln a_{PbSO_4} = d \ln a_{PbS} + 4 d \ln a_{PbO} - 4 d \ln a_{Pb}. \quad\ldots (19)$$

When the right-hand side of equation (19) is inserted into equation (15), the $d \ln a_{PbS}$ terms are eliminated in equations (15) and (16) simultaneously, and the terms are re-arranged, the final equation is

$$\frac{X_{PbO} + 4 X_{PbSO_4}}{X_{PbSO_4}} d \ln a_{PbO} = \frac{X_{Pb} + 4 X_{PbS}}{X_{PbS}} d \ln a_{Pb}. \quad .(20)$$

When both sides of equation (20) are integrated, tie-lines representing the compositions of co-existing melts can be obtained from known activities of Pb and PbO. This is possible because the left-hand side of equation (20) is a function of composition along the PbO-PbSO₄ binary, and the right-hand side is a function of composition along the Pb-PbS binary.

At 1473 K, the sub-regular solution model of Jacob and Toguri[13] yields the following equation for PbO activity in PbO-PbSO₄ melts—see equation (13)—

$$\ln a_{PbO} = \ln X_{PbO} + (1 - X_{PbO})^2$$
$$(- 1,833 - 1,633 X_{PbO}). \quad\quad (21)$$
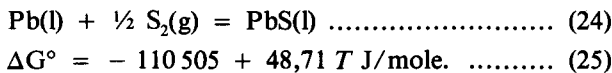
Equation (9) from Eric and Timucin[6] gives the activity of Pb for Pb-PbS at 1473 K as

$$\ln a_{Pb} = \ln X_{Pb} + (1 - X_{Pb})^2 (1,665 - 0,605 X_{Pb}). \quad (22)$$

By differentiating equations (21) and (22) and multiplying by the respective composition terms of equation (20), the final equality after integrating equation (20) is

$$-4\ln\left[\frac{1-X_{PbO}}{X_{PbO}}\right] + 3\ln(1-X_{PbO}) - 4{,}899\ X^3_{PbO} +$$

$$6{,}749\ X^2_{PbO} + 8{,}132\ X_{PbO}\ \bigg|_{\substack{X_{PbO}\ =\ X_{PbO} \\ X_{PbO}\ =\ 0{,}99}}$$

$$= 4\ln\left[\frac{1-X_{Pb}}{X_{Pb}}\right] + 3\ln(1-X_{Pb}) - 1{,}815\ X^3_{Pb} +$$

$$9{,}533\ X^2_{Pb} - 15{,}740\ X_{Pb}\ \bigg|_{\substack{X_{Pb}\ =\ X_{Pb} \\ X_{Pb}\ =\ 0{,}99}}. \quad\quad\quad (23)$$

The integrations were started from X_{PbO} = 0,99 and X_{Pb} = 0,99 to avoid the approach of logarithmic terms to infinity. Except at the very end corners of the composition ranges, the integration is both thermodynamically and analytically sound. Both the left-hand and the right-hand sides of equation (23) are plotted in Fig. 5 as a function of X_{PbSO_4} and X_{PbS} respectively. By the help of this diagram, the end-point compositions of the conjugation lines were determined, and the results are plotted in the Pb–S–O ternary diagram of Fig. 6. The conjugation lines (tie-lines) determined in this manner permit the evaluation of the equilibrium constant, and thus the standard free-energy change for reaction (17). This is possible since all the component activities on each tie-line are known. The mean value of the equilibrium constant at 1473 K is K = 2,019 × 10^{-2} with a variance of 1,078 × 10^{-6}. Then, the standard free-energy change of reaction (17) corresponding to this value of K turns out to be 47 793 ± 630 J. Thus, by use of the standard free energy of formation of liquid PbO from equation (12) and that[3,6] of liquid PbS from equations (24) and (25), the free energy of formation of liquid PbSO₄ is found to be − 315 310 J/mole at 1473 K.

$$Pb(l) + \tfrac{1}{2}\ S_2(g) = PbS(l) \quad\quad\quad\quad\quad (24)$$

$$\Delta G^\circ = -110\,505 + 48{,}71\ T\ \text{J/mole.} \quad\quad\quad (25)$$

With the available free-energy data and the tie-lines determined, the various thermodynamic conditions of lead converting can be mapped quantitatively on a graph of oxygen partial pressure against sulphur partial pressure at constant temperature. This map is shown in Fig. 7. At 1473 K, all the components—Pb, PbS, PbO, and PbSO₄—are molten and, as mentioned previously, the Pb–PbS and PbO–PbSO₄ systems form continuous liquid solutions. The heavy solid lines in Fig. 7 represent the actual phase boundaries between these two liquid solution series, whereas the light solid lines are hypothetical phase boundaries between the pure solid components Pb and PbS on the one hand, and PbO and PbSO₄ on the other. The light dashed lines show the equilibrium conditions between the sulphide and oxy-sulphate melts as a function of the respective activities of PbS and PbO. The constant SO₂ pressure lines were drawn by use of the standard free energy of formation of SO₂ gas[14] at 1473 K.

Another potentially useful type of diagram is shown in Fig. 8, which was constructed with the help of the data provided in Figs. 7 and 6. This diagram depicts the relationships at 1473 K among percentage sulphur, partial pressure, activity of PbS in the metal phase, and activity of PbO in the slag in equilibrium with the metallic phase. Figs. 6 to 8 show clearly that low PbO activity in the slag
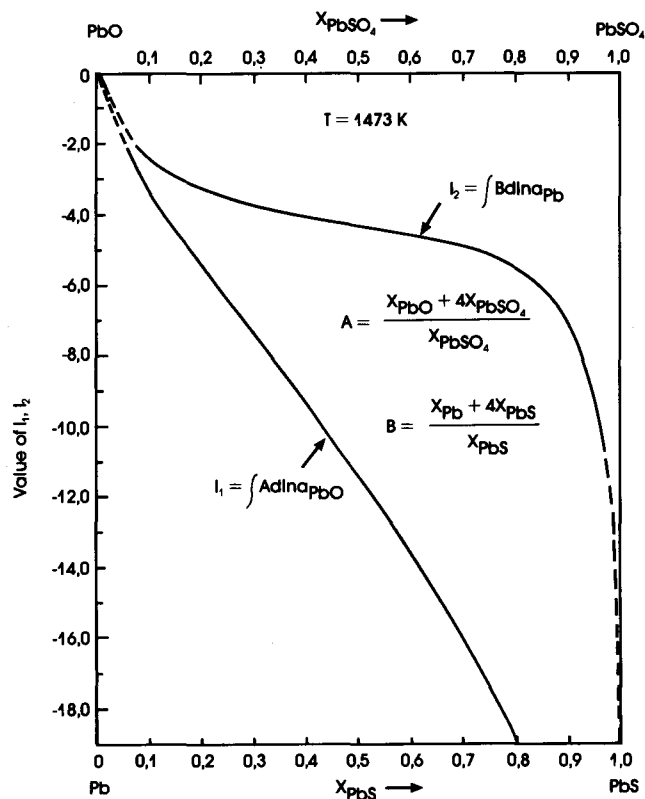

Fig. 5—The integrated values of equation (23) for the derivation of the tie-lines of the system Pb–S–O
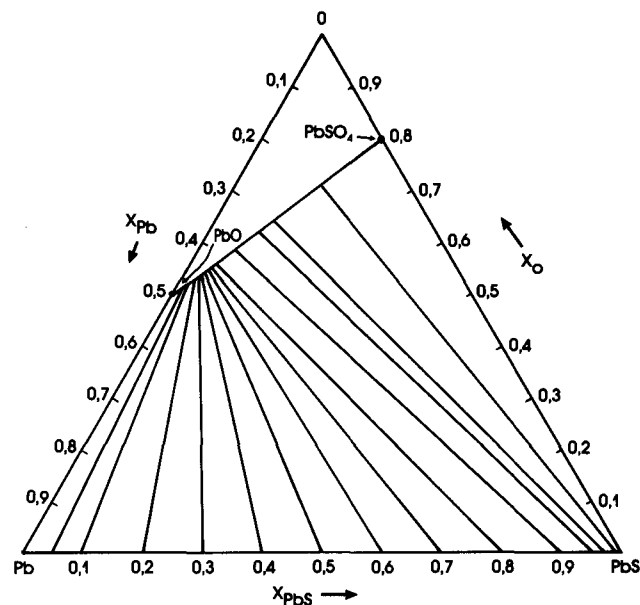

Fig. 6—Tie-lines of the system Pb–S–O at 1473 K, obtained by use of equation (23)

can result in a high percentage of sulphur in the metal and substantial volatilization of PbS; that is, a somewhat incomplete conversion of sulphide to metal.

The conclusions of Schuhmann et al.[3] regarding the Pb–S–O system are qualitiatively in agreement with the conditions pictured here. However, their PbO activities derived at P_{SO_2} = 1,0 atm from the reaction

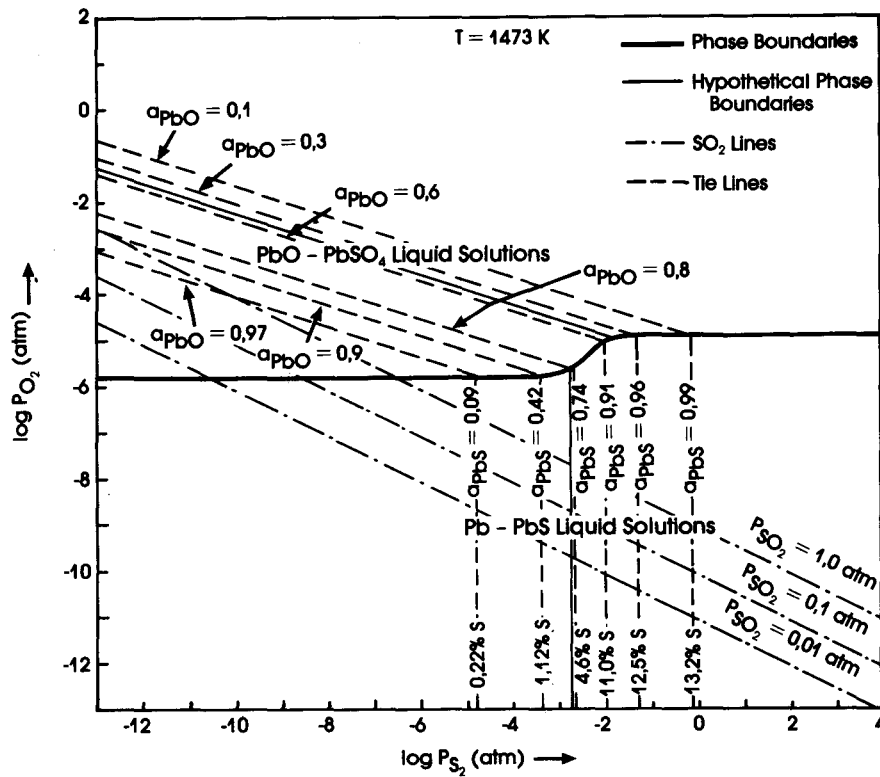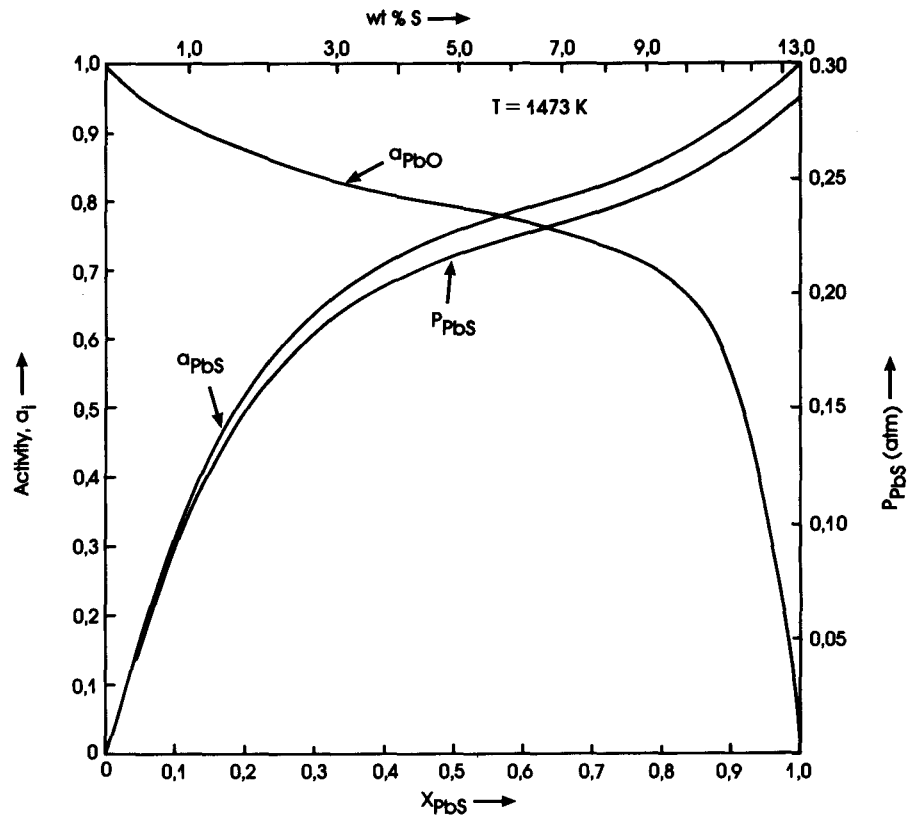$$PbS(l) + 2\ PbO(l) = 3\ Pb(l) + SO_2(g) \quad\quad (26)$$
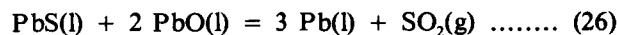
Fig. 7—Isothermal reaction diagram for the system Pb-S-O, showing the equilibrium conditions between Pb-PbS and PbO-PbSO$_4$ liquid solutions at 1473 K

Fig. 8—Equilibrium relations between a_{PbO} (of slag), a_{PbS}, P_{PbS}, and percentage sulphur of the lead bath

are somewhat lower, and do not allow for the presence of PbSO$_4$. The findings of the present investigation are based on reaction (17), which involves the presence of all possible condensed phases pertinent to lead smelting at temperatures in the vicinity of 1200°C. Actually, the

findings of the two studies complement each other. This work shows the equilibria between the metallic sulphide and the oxy-sulphate metals, whereas Schuhmann *et al.*'s work shows the possible variation of PbO activity in the slags as a function of temperature.

Conclusions

A set of consistent thermodynamic and phase-equilibrium conditions is provided for the condensed phase region of the Pb–S–O ternary system. Because of experimental difficulties and a lack of data, some assumptions were made in the analysis of the system. The assumption that the very small mutual solubilities at both ends of the Pb–PbO system at 1473 K could be neglected brings in only insignificant uncertainties to the generated tie-line data. Within these very small solubility regions extending into the ternary-field activity, composition relations definitely follow the same pattern as in the binary PbO–PbSO$_4$ and Pb–PbS systems. However, the other assumption, that the immiscibility region can be extended from the Pb–PbO binary all the way up to the PbS–PbSO$_4$ join may bring in more uncertainties. Although it is estimated that the PbS–PbSO$_4$ system forms an immiscibility region, this definitely needs experimental verification. If these two components do not form immiscibility but rather form continuous liquid solutions, the ternary miscibility gap will close completely within the ternary field before reaching the PbS–PbSO$_4$ join. In such a case, the tie-line distributions near this join will inevitably require modification. Again, this needs experimental confirmation, which is very difficult. However, in the absence of such tests and based on the above assumptions, the analyses presented are sound.

The thermodynamic equilibrium conditions provided in this investigation, in conjunction with stoichiometric and energy-balance considerations, can well serve as a starting point in process design. A single-stage converting or direct-smelting process for PbS concentrates necessitates an optimum balance between the PbO content of the slag and the sulphur content of the lead bullion. It seems justified that, to avoid substantial volatilization of PbS and to achieve relatively efficient conversion of PbS to Pb, high PbO activities in the slag must be considered. For example, the supply of oxygen can be regulated to produce a slag of high PbO content (a_{PbO} about 0,9) and a lead product of intermediate sulphur content (about 1,1 per cent). However, with such a compromise, both the crude metal and the slag will require further processing, and high-purity concentrates will be necessary. If substantial quantities of gangue must be removed in the slag, PbO activity will be lowered, and thus efficient conversion of PbS to PbO will not take place. In such a case, a suitable fluxing agent that will increase the activity coefficient of PbO in the slag is needed. Furthermore, the Pb–PbS bath must be well mixed to avoid extensive local over-oxidation[6] because there is no immiscibility in this system; that is, Pb will not separate from PbS and sink to the bottom of the reactor as in copper converting.

It is noteworthy that a multizone reactor or a multistage process can afford better conditions for direct lead smelting. For example, a countercurrent flow of metal and slag phases in a reactor with sequential staging of the controlling physicochemical conditions can produce a crude metal of low sulphur content at the metal-discharge end by oxygen injection, which will increase a_{PbO} to high values. Towards the slag discharge-end, reducing conditions can be provided with a deficiency of oxygen and with reducing agents to bring the PbO content of the slag to an acceptably low value. Along the length of the reactor, intermediate conditions can be achieved by staged additions of concentrates and other feed materials to follow an optimum path.

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Preconcentration and cyanidation by P.J.D. Lloyd*

In a letter to the Editor, Dr Lloyd writes as follows.

The publication by the Institute of *The Extractive Metallurgy of Gold in South Africa*[1] is a landmark in the long history of such texts. Nevertheless in one area I believe it to be deficient, namely the lack of accent on gravity or other preconcentration procedures relative to cyanidation. In the 1970s it was estimated that 43 per cent of all the gold produced in South Africa arose from amalgamation[2] and, while amalgamation has, for environmental reasons, been superseded, the fact remains that a large proportion of the gold is not recovered by direct cyanidation of the whole ore.

Indeed, Penman[3] in his chapter on gravity concentration notes 'The desirability or otherwise of employing gravity concentration in addition to cyanidation in the treatment of the non-refractory Witwatersrand-type ores has been a bone of contention ever since the introduction of the cyanide process in 1890'. It is the purpose of this note to offer a simple theorem by which the merits of preconcentration procedures can be judged.

Consider an ore, head grade H g/t, of which F g/t can be concentrated and then recovered by a process having an overall fractional recovery of R_F. Let R_H be the fractional recovery by cyanidation of the whole ore and R_R be the fractional recovery by cyanidation of the ore remaining after removal of the concentrate. Then it can be shown simply that overall recovery is improved whenever

$$R_R > \frac{R_H - R_F \cdot F/H}{(1 - F/H)} . \qquad (1)$$

Now many concentration treatments, e.g. amalgamation, intensive cyanidation, fine milling of a pyrite concentrate followed by cyanidation of both concentrate and calcine, have very high recoveries; that is $R_F > 0,99 \simeq 1,00$. Thus, to a good approximation, inequality (1) can be closely approximated by

$$R_R > \frac{R_H - F/H}{(1 - F/H)} . \qquad (2)$$

This relationship is shown for the parameter F/H, the fraction of gold in the head that reports to the concentrate, in Fig. 1.

What this demonstrates is that, *if there are two competing processes of differing efficiency and the process of higher efficiency can be applied to only a part of the feed, then the efficiency of the less efficient process can be dropped markedly, and the greater the proportion of the valuable constituent that can be diverted to the higher-efficiency process.*

Two numerical examples can illustrate the point further. Consider first gravity concentration, followed by cleaning of the concentrate before intensive cyanidation. Assume $F/H = 10$ per cent, $R_H = 0,965$, and $R_R = 0,995$. Then $R_c > 0,9617$, i.e. because R_H is low, there is little benefit. Now consider flotation of pyrite in the mill circuit, fine milling of the pyrite concentrate, cyanidation, and re-cyanidation of the pyrite calcine. Assume $F/H = 80$ per cent, $R_H = 0,965$, and $R_R = 0,985$. Then $R_c > 0,885$, i.e. because F/H is high, the efficiency of

cyanidation of the remainder of the ore can be allowed to drop markedly.

All these aspects have been proved in practice. For instance, Brittan[4] showed that the overall efficiency of the plants in the Anglo American group could be improved the greater the proportion of gold recovered by gravity concentration. Bushell[5] showed that the introduction of flotation into the mill circuit at Hartebeestfontein permitted an increase in tonnage, a coarsening of the overall grind, and a reduction in cyanide-leaching time with an improvement in overall recovery.

I believe these issues should now be resolved, and Penman's 'bone of contention' finally discarded, even if it has taken us 98 years to chew through it!
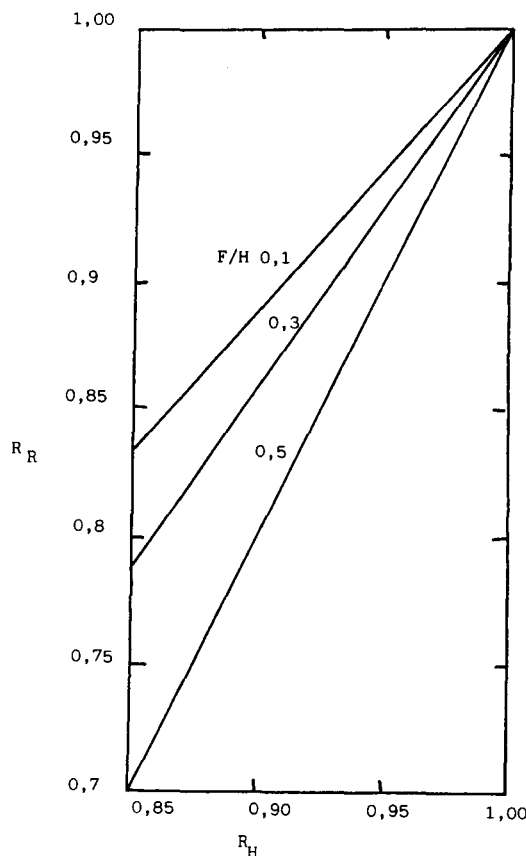

Fig. 1—Minimum value of cyanidation recovery, R_R, as a function of whole ore recovery, R_H, with parameter F/H, fraction of the total gold recovered from the feed in the gravity or other concentrate

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