Technical note

Behaviour of copper in refining of lead by fractional crystallization

K. Qiu, Q. Chen, P. Winkler and J. Krüger

Before the Parkes process for lead refining was developed the Pattinson process had been used for 80 years. The Pattinson process is based on metal refining by fractional crystallization from the melt and has been described in numerous works from the 1820s onwards. For a long time it was considered that some copper reports to the Pb–Ag alloy and some to the lead crystals, with the result that copper cannot be removed from the lead melt by this process, i.e. by fractional crystallization.[1–4] As this conclusion is incompatible with the phase diagram for Pb–Cu binary system, a new investigation of the topic has been undertaken.

Theoretical analysis

Fractional crystallization from the melt is possible only if the solute concentration in the solid differs from that in the liquid with which the solid is at equilibrium. The behaviour of the metals in the process of metal refining by fractional crystallization can be predicted from the phase diagram. With reference to Fig. 1, when melt L containing impurity B (b_L, %B) is cooled to temperature T_1 the crystal b_1 is at equilibrium with the B-enriched liquid, b_1'. If the crystal b_1 is separated from the liquid b_1', a solid phase, b_1, is the first refined product. When the obtained solid phase b_1 is reheated to temperature T_2 the crystal b_2, which has a lower content of impurity B than crystal b_1, is at equilibrium with liquid b_2', which contains less B than did liquid b_1'. If the process is repeated, the impurity in the crystal becomes less and less and, eventually, pure metal can be produced until the impurity (B) content in the liquid phase reaches or is close to the eutectic point, b_E (see Fig. 1).

The important observation from the phase diagram for the Pb–Cu binary system (Fig. 2) is that the behaviour of copper in the refining of lead by fractional crystallization is related to its content. If the copper content in the lead melt is less than that in a eutectic mixture at 326°C, copper should be removed during the lead refining by fractional crystallization as in the Pattinson process.

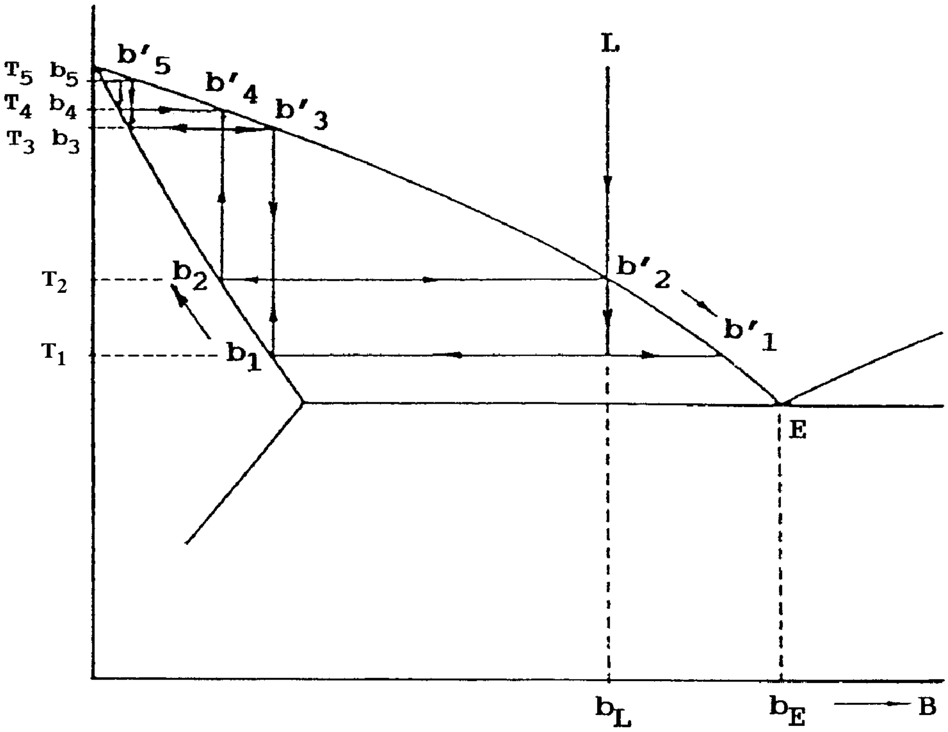

Fig. 1. Schematic diagram of metal refining by fractional crystallization; *see text for explanation*

Experimental materials and apparatus

All experiments were carried out in the Institute of Nonferrous Process Metallurgy at Aachen University of

Table 1 Chemical composition of crude lead—impurity contents

Per cent								ppm
Ag	Sb	Sn	As	Cu	Zn	Ni	Bi	Cd
0.148	0.106	0.00059	0.0024	0.240	0.00058	0.0012	0.072	<5

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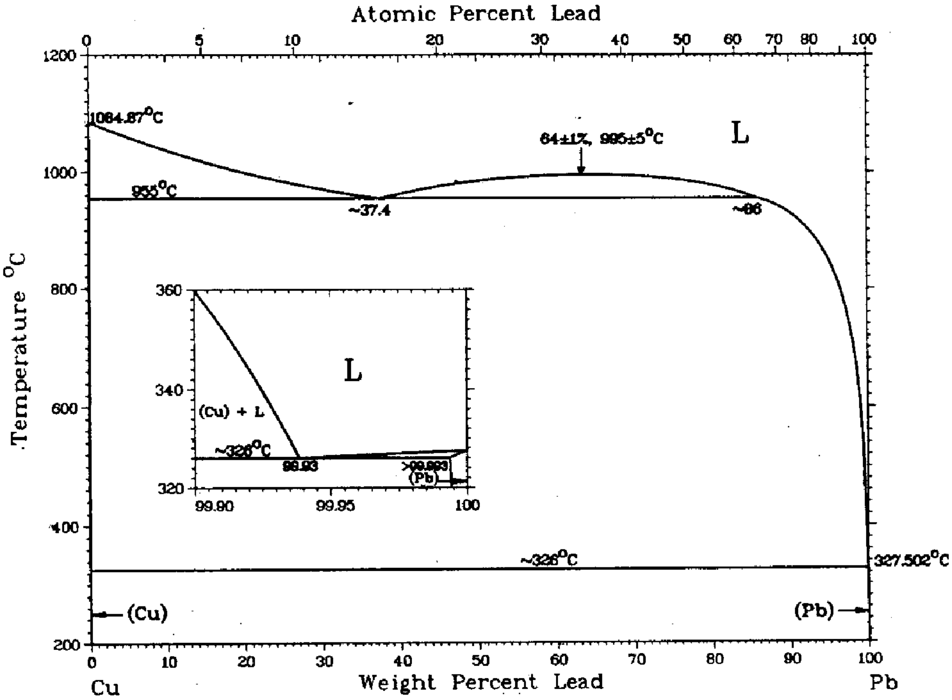

Fig. 2 Phase diagram for Pb-Cu binary system[5]

Technology, Germany. Crude lead for use in the experiments was supplied by a German smelter and its chemical composition is given in Table 1.

The experimental apparatus was a continuous crystallizator (Fig. 3). It consists of two principal parts: electric heaters and a spiral separator. Metal refining by the continuous crystallizator may be regarded as an improved Pattinson process that operates simultaneously and continuously to produce a solute-enriched liquid and purified crystals from the two ends.[6,7] The continuous crystallizator was heated by four sets of electric heaters such that the temperature gradient in the melt could be controlled to adhere closely to the phase diagram. The design of the apparatus also creates good conditions for the countercurrent separation of the solid and liquid phases by enabling adjustment of the rotational speed of the spiral separator and the inclination of the crystallizator. The course of refining was monitored via thermocouples placed in the low end, the middle and the high end of the crystallizator.

Results and discussion

The results of the first part of the experiments showed that when the copper content in the lead melt is greater than that in a eutectic mixture (*ca* 326°C) some copper reports to the Pb–Ag alloy and some to the lead crystals, so that the purified lead always contains some copper. This is in accordance with reports in the literature and conforms to the phase diagram for the Pb–Cu binary system. Therefore, only the behaviour

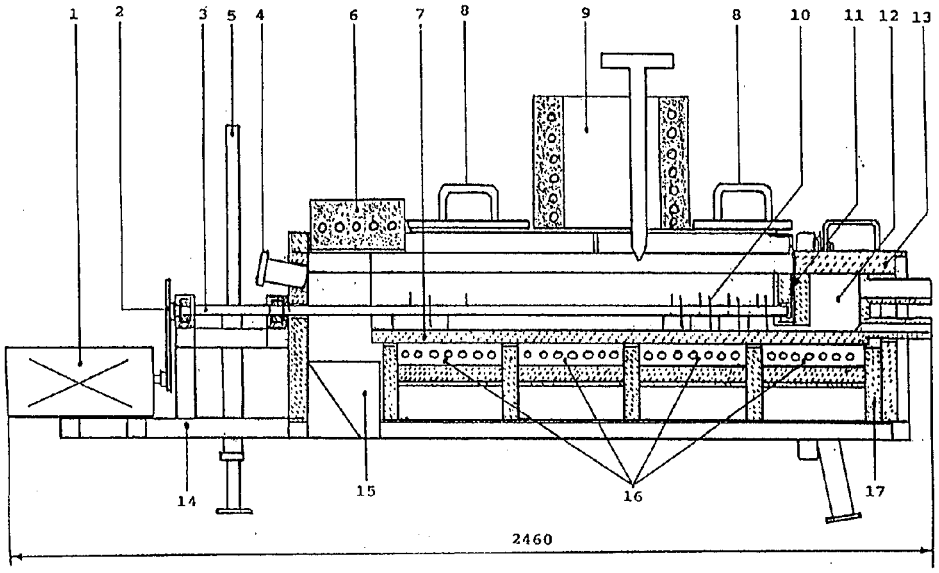

Fig. 3 Continuous crystallizator: *1*, motor; *2*, transmission; *3*, screw axis; *4*, lamp; *5*, inclination regulator; *6*, supplementary heater; *7*, trough (SiC-lined); *8*, cover; *9*, charge pot; *10*, spiral blade; *11*, partition wall; *12*, melt syphon and outlet; *13*, refractory cover; *14*, chassis; *15*, outlet for crystals; *16*, heaters; *17*, refractory wall

of copper constituting less than 0.07% of the lead melt is discussed here.

In these experiments the crude lead (cf. Table 1) was treated with sulphur to reduce its copper content to less than 0.07% and it was then refined by the crystallizator. Table 2 presents the results for the removal of copper, bismuth and silver. In Table 2 'Removal' is defined as 100 × (Impurity content in feed – Impurity content in product of refining) ÷ Impurity content in feed.

Table 2 Experimental results

Material	Composition, % Cu	Bi	Ag
Feed	0.037	0.071	0.154
Product of refining	0.001	0.027	0.003
Ag-enriched liquid	0.063	0.157	0.667
Removal, %	97.3	61.97	98.05

The results for Cu, Bi and Ag removal are also presented in Figs. 4 and 5 from other experimental data. Fig. 4 shows that copper in refined lead crystals can be removed progressively by the continuous crystallizator. About 6 h was required for the desired temperature gradient and concentration gradient in the melt to be reached, after which copper was essentially removed from the lead crystals and lead crystals were taken as the product from the high end of the crystallizator.

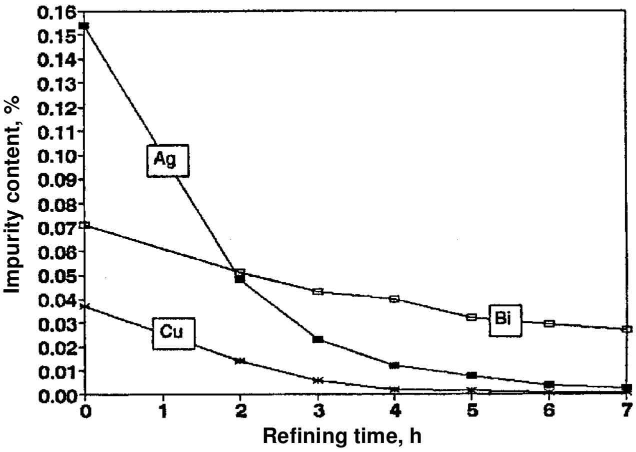

Fig. 4 Relationship between impurity content in refined lead and refining time

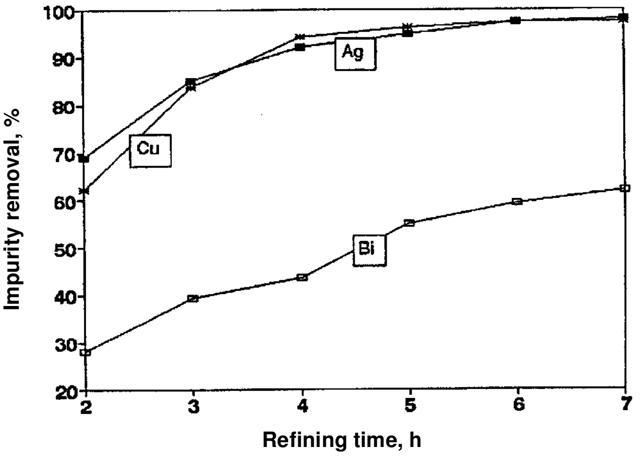

Fig. 5 Relationship between refining efficiency and refining time

Fig. 5 shows that the removal of copper is much better than that of bismuth and similar to that of silver. The results in Table 2 show minima of 0.001, 0.027 and 0.003% for copper, bismuth and silver, respectively, in the refined lead, and maxima of 0.063, 0.157 and 0.667% for copper, bismuth and silver, respectively, in the impurity-enriched liquid. It is concluded that a high degree of removal of copper impurity from the lead melt by fractional crystallization is not a problem when the copper content of the feed is less than 0.07%, but the behaviour of copper when its content exceeds 0.07% is entirely different.

Conclusion

The experimental results all showed that when the copper content in the lead melt is greater than 0.07% some copper reports to the Pb–Ag alloy and some to the lead crystals, with the result that the purified lead always contains some copper. However, when the copper content in the lead melt is less than 0.07% copper can be removed satisfactorily by fractional crystallization, becoming enriched in the silver-containing liquid. The behaviour of copper in the refining of lead by fractional crystallization is thus related to its content. The experimental results accord with the phase diagram for the Pb–Cu binary system.

References

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Correction

Diffusion of oxygen in liquid copper and nickel

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In the last two full lines of the synopsis *E* is oxygen diffusion activation energy/mol—that is, the following 'K' was included in error. On page C82 the unit of *D* should have been given as metres^2 per second; unfortunately, the power 2 was omitted.