

MARIAN KUCHARSKI*, WIESŁAW MRÓZ*, JANUSZ KOWALCZYK*,
MARIAN WARMUZ**, PIOTR ROMANOWICZ**,
JERZY GARBACKI**, GRZEGORZ SZWANCYBER**

LEAD REMOVAL FROM Cu-Pb-Fe ALLOYS BY GAS INJECTION INTO MELT

USUNIĘCIE OŁOWIU ZE STOPÓW Cu-Pb-Fe W WYNIKU PRZEPUSZCZANIA GAZU PRZEZ STOP

In KGHM copper smelters, two processes are used for blister production. First is a conventional one with matte converting stage, and second is the Outokumpu single-stage process. In both processes, Polish concentrates are used, which comprise also considerable amount of lead.

In the Outokumpu single-stage process approximately 1/3 of the copper reports to the slag, and therefore slag cleaning process in the electric furnace is employed. In consequence Cu-Pb-Fe alloys are obtained. These alloys have to be converted what creates enormous problems with converter lining corrosion caused by lead oxide, which increase operational costs. A possible solution to this problem could be the lead removal from the Cu-Pb-Fe alloys by injection into melt oxidising gas of certain oxygen potential. The process should be carried out practically without slag phase. The bubble travelling through the bath are saturated by lead vapour which then is oxidised. As an effect the lead is removed from the liquid to flue dust in form of lead and lead oxide.

The results of the laboratory tests and thermodynamic consideration concerning this problem are presented.

W hutach miedzi KGHM „Polska Miedź” SA stosuje się dwa procesy do otrzymywania miedzi blister. Jeden z nich jest procesem konwencjonalnym, a drugi jest technologią firmy Outokumpu jednostopniowego otrzymywania miedzi. W obu procesach przetwarzane koncentraty miedzi zawierają znaczne ilości ołowiu. W procesie zawieszinowym ołów przechodzi głównie do żużla, który jest następnie odmiedziowywany w piecu elektrycznym. W procesie odmiedziowania żużli zawieszinowych oprócz miedzi wydziela się także żelazo i ołów tworząc stopy Cu-Pb-Fe.

* WYDZIAŁ METALI NIEŻELAZNYCH, AKADEMIA GÓRNICZO-HUTNICZA, 30-059 KRAKÓW, AL. MICKIEWICZA 30

** HUTA MIEDZI GŁOGÓW, 67-231 ŻUKOWICE, POLSKA

Praca miała na celu określenie optymalnych warunków do odpędzenia ołowiu z tych stopów praktycznie bez udziału fazy żuźlowej. Idea tego procesu polega na przepuszczaniu gazu obojętnego lub o niewielkim potencjale tlenowym przez ciekły stop, w wyniku czego pęcherzyki gazu nasycają się parami ołowiu, które z kolei podlegają procesowi utleniania. W efekcie ołów jest odpędzany do pyłów w postaci ołowiu oraz tlenku ołowiu. Obliczenia termodynamiczne wskazują na możliwość odpędzenia ołowiu ze stopów Cu-Pb-Fe za pomocą proponowanego procesu. Usuwanie ołowiu poprzez konwertorowanie stopów Cu-Pb-Fe jest procesem uciążliwym i przede wszystkim bardzo kosztownym. Przeprowadzone badania potwierdziły przewidywane tendencje wzrostu efektywności odpędzania ołowiu w miarę wzrostu potencjału tlenowego przepuszczanego przez kąpiel gazu.

1. Introduction

The injection of gases into melts is one of the most important operations in the metallurgical industry. This operation is used in converters, zinc fumers, anode furnaces and many other processes. Gas injection into liquid results in the formation of bubbles that promote reactions, mixing as well as mass and heat transfer. The elimination of the lead from Cu-Pb-Fe alloys in the form of Pb and PbO vapour could be an example of such process. Figure 1 shows the situation in which lead diffuses to formed bubble of nitrogen which then rises through the Cu-Pb-Fe alloy. The bubble is saturated by lead vapour according to the reaction:

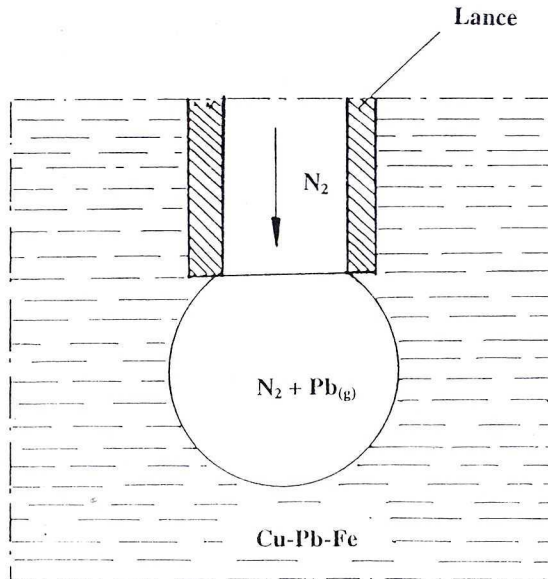


Fig. 1. Saturation of the gas bubble by evaporated lead from the Cu-Pb-Fe alloy

The lead vapour pressure can be estimated from the relation:

$$P_{\text{Pb}} = P_{\text{Pb}}^0 \cdot a_{\text{Pb}(\text{CuPbFe})}, \quad (2)$$

where: P_{Pb} — is the lead vapour pressure over Cu–Pb–Fe alloy; P_{Pb}^0 — is the lead vapour pressure over pure liquid lead; $a_{\text{Pb}(\text{CuPbFe})}$ — is the activity of the lead in the Cu–Pb–Fe alloy.

2. Thermodynamic model for the lead removal process from Cu–Fe–Pb alloys

The knowledge of the activity coefficient of the lead in Cu–Pb–Fe alloys enables us to compute its activity and then the lead vapour partial pressure over these alloys. Lead activities coefficients can be determined from the relation given by W y p a r - t o w i c z [1]:

$$\begin{aligned} \ln \gamma_{\text{Pb}} = & \left(\frac{5063.88}{T} - 1.342 \right) [(1 - X_{\text{Cu}})^{2.098} - 1.911(1 - X_{\text{Cu}})^{1.098} + \\ & + X_{\text{Cu}}(1 - X_{\text{Cu}})^{0.098} X_{\text{Fe}} + 0.911] + \left(\frac{-2211.175}{T} + 1.078 \right) \times \\ & \times [(1 - X_{\text{Cu}})^{3.098} - 1.477(1 - X_{\text{Cu}})^{2.098} + X_{\text{Cu}}(1 - X_{\text{Cu}})^{1.098} X_{\text{Fe}} + 0.477] - \\ & - \left(\frac{4146.95}{T} + 0.361 \right) X_{\text{Cu}} X_{\text{Fe}} (1 - X_{\text{Fe}})^{0.012} - \left(\frac{396.17}{T} - 0.965 \right) \times \\ & \times X_{\text{Cu}} X_{\text{Fe}} (1 - X_{\text{Fe}})^{1.012} + \left(\frac{26431.492}{T} - 5.149 \right) \times \\ & \times [(1 - X_{\text{Fe}})^{2.033} - 1.968(1 - X_{\text{Fe}})^{1.033} + X_{\text{Fe}}(1 - X_{\text{Fe}})^{0.033} X_{\text{Cu}} + 0.968] + \\ & + \left(\frac{-16357.443}{T} + 4.675 \right) [(1 - X_{\text{Fe}})^{3.033} - 1.492(1 - X_{\text{Fe}})^{2.033} + \\ & + X_{\text{Fe}}(1 - X_{\text{Fe}})^{1.033} X_{\text{Cu}} + 0.492] \end{aligned} \quad (3)$$

In the case when injected gas into the melt contains oxygen, then the lead vapour in the bubble would be oxidised until the equilibrium of the oxidising reaction is reached:



The vapour pressure of the lead oxide in the bubble can be determined from the equilibrium constant:

$$P_{\text{PbO}} = K \cdot P_{\text{Pb}} \cdot P_{\text{O}_2}^{0.5}, \quad (5)$$

where: K is the equilibrium constant, P_{O_2} — the partial pressure of oxygen in the bubble which for some extent can be controlled by oxygen content in injected gas. Under assumption that the gas in the bubble behaves ideally, “ n_i ” lead moles evaporated from the Cu–Fe–Pb alloy occupy the volume “ V_i ” in which partial pressures of lead and lead oxide attained equilibrium values.

$$V_i \cdot (P_{Pb} + P_{PbO}) = (n_{Pb} + n_{PbO}) \cdot R \cdot T. \quad (6)$$

If $n_i = n_{Pb} + n_{PbO}$ is small enough, then we can assume that the composition of the alloy remains almost unchanged during evaporation this portion of lead. In such case, the partial pressure of lead over Cu–Pb–Fe alloy can be regarded as nearly constant. Let us assume that the lead concentration in the alloy at the beginning of the process is y_{Pb}^0 expressed in wt.%, while the final content of the lead should be equal y_{Pb}^f (0.2, 0.3, 0.5 or 1 wt.%). The mass of lead to be evaporated is given by the relation:

$$m = m_0 \left[\frac{y_{Pb}^0}{100} - \frac{y_{Pb}^f \left(1 - \frac{y_{Pb}^0}{100} \right)}{100 - y_{Pb}^f} \right], \quad (7)$$

where: m_0 is total mass of the alloy before the evaporation process.

Next, we divide arbitrarily this mass into “ n ” (n could be taken for example 100, 200, ...) equal parts. Under this assumption a number of moles “ n_i ” may be expressed as:

$$n_i = \frac{m}{207.2 \cdot n}. \quad (8)$$

To accommodate n_i ($n_i = n_{Pb} + n_{PbO}$) moles of lead in the form of metal and oxide saturated vapour; the volume V_i of the injected gas has to be used:

$$V_i = \frac{n_i \cdot R \cdot T}{P_{Pb} + P_{PbO}}. \quad (9)$$

After evaporation of “ n_i ” lead moles, the alloy composition is altered:

$$\begin{aligned} X_{Pb}^i &= \frac{n_{Pb}^{i-1} - n_i}{n_{Cu}^0 + n_{Fe}^0 + n_{Pb}^{i-1} - n_i} \\ X_{Cu}^i &= \frac{n_{Cu}^0}{n_{Cu}^0 + n_{Fe}^0 + n_{Pb}^{i-1} - n_i} \\ X_{Fe}^i &= 1 - X_{Pb}^i - X_{Cu}^i, \end{aligned} \quad (10)$$

where: n_{Pb}^{i-1} is the number of moles of lead in the alloy before evaporation of n_i moles of lead, n_{Cu}^0 and n_{Fe}^0 are the number of moles of copper and iron respectively. It was

assumed that n_{Cu}^0 and n_{Fe}^0 does not change during the process for low oxygen pressures.

Taking into account this alloy composition, new values of γ_{Pb}^i , P_{Pb}^i and P_{PbO}^i were determined. These quantities were used to compute a new value of V_i according to equations (3), (2), (5) and (9). This procedure was repeated until the final concentration of lead in the alloy was reached. By summation over all V_i , total volume of the gas needed to remove the required amount of lead can be computed. In the present work such computations were carried out at 1300°C and 1400°C for gases having various oxygen pressures.

For example, when blast is made up with air and CO, mass balance for oxygen, carbon, and nitrogen as well as two additional conditions are employed. These conditions are:

1. the total pressure in the system is set up to be 1 bar,
2. the equilibrium between carbon monoxide, carbon dioxide and oxygen is assumed.

In this case a set of five linear equations should be solved:

$$\begin{bmatrix} (\text{O})_{\text{PbO}} \\ 0 \\ 0 \\ 1 - P_{\text{Pb}} - P_{\text{PbO}} - P_{\text{O}_2} \\ 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0.57 & -0.57 & -0.73 \\ 0 & 0 & -0.43 & 0.43 & 0.27 \\ 329 & -1 & 0 & 0 & 0 \\ 0 & \frac{1000 RT}{28 V_i} & 0 & \frac{1000 RT}{28 V_i} & \frac{1000 RT}{44 V_i} \\ 0 & 0 & 0 & K \cdot P_{\text{O}_2}^{0.5} & -1 \end{bmatrix} \cdot \begin{bmatrix} (\text{O}_2)_b \\ (\text{N}_2)_b \\ (\text{CO})_{\text{off}} \\ (\text{CO})_b \\ (\text{CO}_2)_{\text{off}} \end{bmatrix} \quad (11)$$

where: $(\text{O}_2)_b$, $(\text{N}_2)_b$, $((\text{N}_2)_b = (\text{N}_2)_{\text{off}})$, $(\text{CO})_b$, $(\text{CO})_{\text{off}}$, $(\text{CO}_2)_{\text{off}}$ are unknown amounts of gases in blast and off-gas, K is equilibrium constant for the reaction $\text{CO} + 0.5 \text{O}_2 \rightarrow \text{CO}_2$, P_{O_2} — is a final oxygen pressure in the off-gas. In the case when the blast consists entirely of carbon monoxide and air in different proportions, the amount of blast that is required to remove the lead from Cu–Pb–Fe alloys can be computed. The results of these calculations are shown in Figs 2 and 3.

It can be easily noticed that amount of the blast needed to remove the same lead quantity from the Cu–Pb–Fe alloys is considerably smaller than in this case in comparison with use of pure nitrogen.

In reality the travelling time of the bubbles through the melt is too short to be saturated with Pb or PbO vapour. In consequence more blast gases are needed to achieve the objective. To demonstrate a gap between theoretical and practical rate of the process, the lead removal coefficient from the alloys was defined by the expression:

$$\alpha = \frac{m_{\text{Pb}}^0 - m_{\text{Pb}}^i}{m_{\text{Pb}}^0}, \quad (12)$$

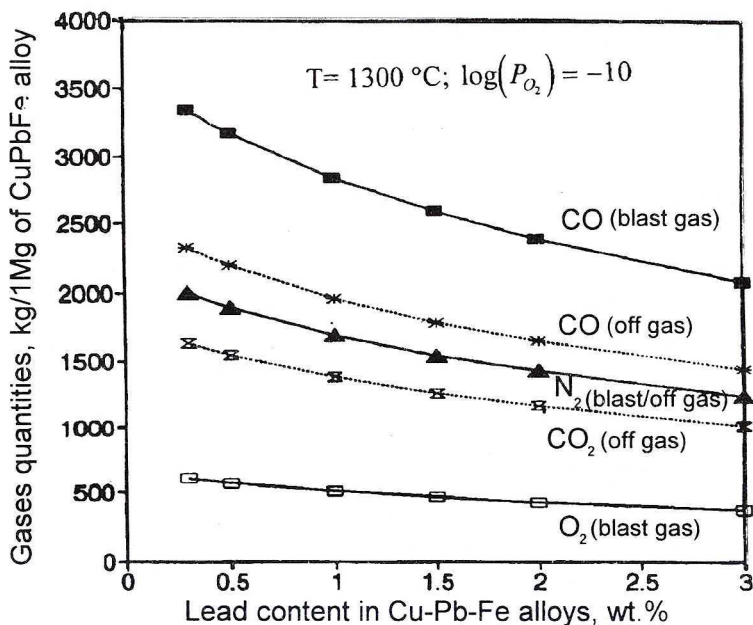


Fig. 2. The relations between amounts of gases in blast (O_2 , N_2 , CO) and in off-gases (N_2 , CO , CO_2) and lead final concentration in the Cu-Fe-Pb alloy. The oxygen pressure in the leaving bath bubbles is 10^{-10} atm. at 1300°C

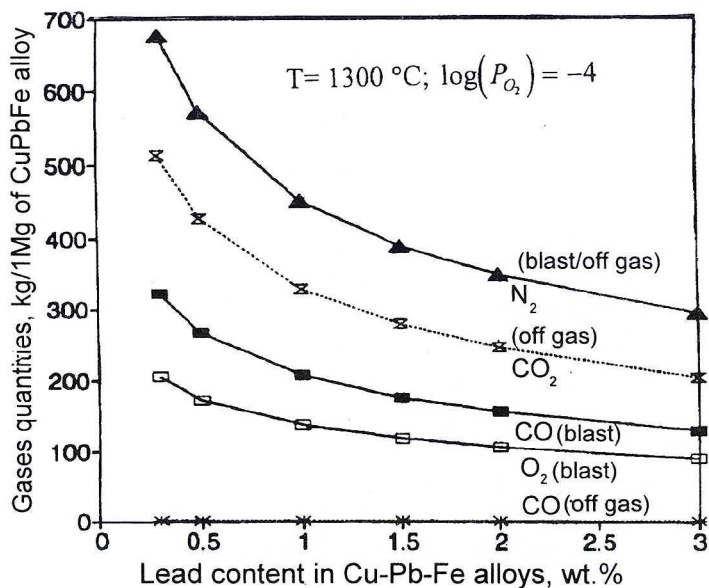


Fig. 3. The relations between amounts of gases in blast (O_2 , N_2 , CO) and in off-gases (N_2 , CO , CO_2) and lead final concentration in the Cu-Fe-Pb alloy. The oxygen pressure in the leaving bath bubbles is 10^{-4} atm. at 1300°C

where: m_{pb}^0 — mass of the lead in the Cu–Pb–Fe alloy before the process, m'_{pb} — mass of the lead in the Cu–Pb–Fe after bubbling during time “ t ”.

3. Results obtained during injection of pure nitrogen into Cu–Fe–Pb alloys

Alloys employed in the experimental work were supplied by HM “Glogow” plant in form of slabs, which compositions varied considerably (Pb 13.4–21.2 wt.%, Fe 1–4% wt.%). Cu–Pb–Fe samples of 920–970 g were placed in alumina crucibles with dimensions: internal diameter 52 mm, and 90 mm high. The crucible with the sample was put into outer graphite crucible, which was situated in the furnace. Next the furnace was switched on, and after equilibration at the desired temperature, the nitrogen was introduced into the melt with a lance made of alumina. An overpressure in the furnace chamber was set up by nitrogen to limit oxidation of the outer crucible. The flowrate of the bubbling gas was maintained at constant level. Figure 4 shows the schematic representation of the apparatus.

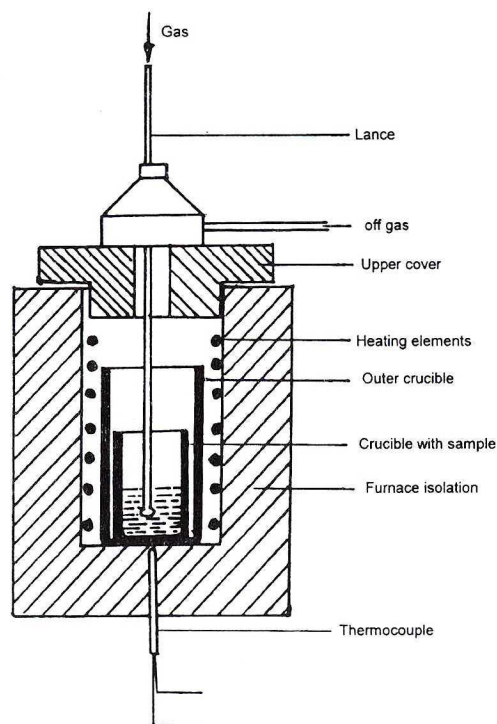


Fig. 4. Schematic diagram of the experimental apparatus

During gas bubbling, the metal samples were taken by sucking with quartz tubes. The samples were analysed for lead. The iron content was determined in the samples

before and after experiments. In order to determine influence of the dispersion of the gas on lead removal coefficient, the same gas amount was also injected into melt through three lances. Tables 1 and 2 give the results obtained for pure nitrogen injection.

The iron content in the alloys before and after experiments with nitrogen use was the same.

TABLE 1

The results of the lead removal from Cu-Pb-Fe alloys by nitrogen injection. The gas was introduced into the melt through one lance

Time, min	$T = 1300^{\circ}\text{C}$; 50 l/h wt.% Pb in alloy	$T = 1400^{\circ}\text{C}$; 50 l/h wt.% Pb in alloy
0	15.39	20.98
30	14.96	20.97
60	14.75	21.10
90	14.39	21.23
120	14.46	21.08
180	14.54	20.96
240	14.25	20.31
300	14.26	20.13

TABLE 2

Experimental results obtained during nitrogen injection into Cu-Pb-Fe alloys. Nitrogen with flowrate 50 l/h was introduced through three lances

Time, min	$T = 1300^{\circ}\text{C}$; 25 l/h wt.% Pb in alloy	$T = 1300^{\circ}\text{C}$; 50 l/h wt.% Pb in alloy	$T = 1400^{\circ}\text{C}$; 25 l/h wt.% Pb in alloy	$T = 1400^{\circ}\text{C}$; 50 l/h wt.% Pb in alloy
0	21.79	14.90	15.46	16.07
30	22.08	14.55	15.39	16.10
60	21.65	14.59	15.18	15.58
90	21.11	14.37	14.96	15.09
120	21.56	14.24	14.73	14.68
180	21.87	14.00	13.96	13.73
240	21.47	13.81	13.49	12.74
300	20.79	13.23	13.13	12.02

4. Results obtained during injection of carbon dioxide into Cu-Pb-Fe alloys

Carbon dioxide can be used to generate the oxygen according to the reaction:



This oxygen can oxidise the lead vapour to form lead oxide and in this way to speed up the lead removal from the alloy.

The experimental procedure was exactly the same as in previous case. However, bubbles were formed by carbon dioxide injected into the melt. The flow rate of the

CO₂ gas was maintained at constant level. Then the alloy was sampled with quartz tubes and analysed for lead. The results are enclosed in table 3.

The iron was almost completely oxidised during these experiments.

TABLE 3

The results of the lead removal from Cu-Pb-Fe alloys by CO₂ injection with various flowrates at 1300°C and 1400°C. The gas was introduced into the melt through three lances

Time, min	$T = 1300^{\circ}\text{C}$; 25 l/h wt.% Pb in alloy	$T = 1300^{\circ}\text{C}$; 50 l/h wt.% Pb in alloy	$T = 1400^{\circ}\text{C}$; 25 l/h wt.% Pb in alloy	$T = 1400^{\circ}\text{C}$; 50 l/h wt.% Pb in alloy
0	18.35	21.10	13.42	14.94
30	19.10	19.76	—	13.74
60	18.72	20.52	13.62	13.64
90	18.55	20.05	12.87	13.28
120	18.14	20.41	11.30	12.89
180	17.57	18.84	11.57	11.86
240	17.02	18.20	10.51	10.60
300	17.34	17.84	10.27	9.69

5. Results obtained during injection of air-propane/butane mixture into Cu-Pb-Fe alloys

Experimental procedure employed in this case was exactly the same as for nitrogen and carbon dioxide. Compositions of air-propane/butane mixtures were made up assuming that oxygen in the air oxidised stoichiometrically propane and butane. The flow rate of the gas mixture into alloys was maintained and controlled at constant level. During gas bubbling, the metal samples were taken by sucking with quartz tubes. These samples were analysed for lead. Obtained results are enclosed in table 4.

It was found that during these experiments, the iron in the alloys was oxidised.

TABLE 4

The results of the lead removal from Cu-Pb-Fe alloy during air-propane/butane injection into melts. The gas was introduced into the melt through one lance

Time, min	$T = 1300^{\circ}\text{C}$; 50 l/h wt.% Pb in alloy	$T = 1400^{\circ}\text{C}$; 50 l/h wt.% Pb in alloy
0	18.98	21.23
30	18.37	20.24
60	16.96	19.50
90	17.60	18.50
120	17.86	17.88
180	17.12	16.01
240	15.60	15.20
300	14.46	12.90

All results were described by the linear equations (see Fig. 5) $\text{wt.\% Pb} = a - b \cdot t$, and then the lead removal coefficients were estimated from the relation:

$$\alpha \approx \frac{b \cdot t}{a} \cdot 100\% . \quad (14)$$

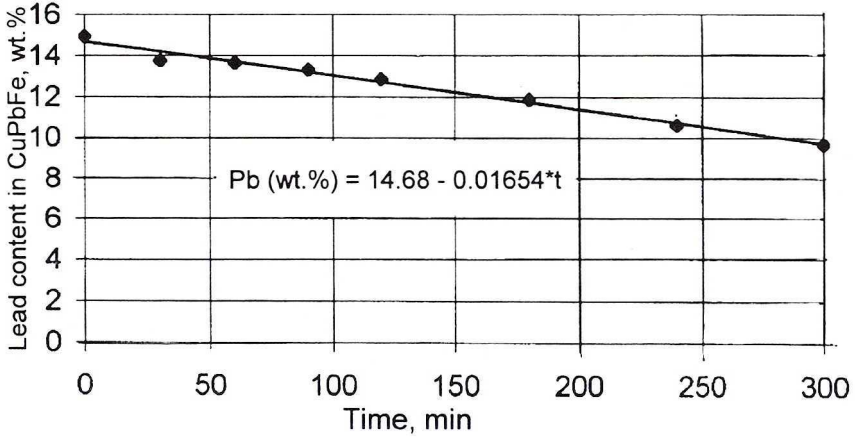


Fig. 5. Dependence of lead content in the Cu-Pb-Fe alloys and time at 1400°C. The blast gas was CO_2 at flowrate 50 l/h

In Fig. 6 the lead removal coefficients for employed gases were plotted as a function of process time at 1400°C.

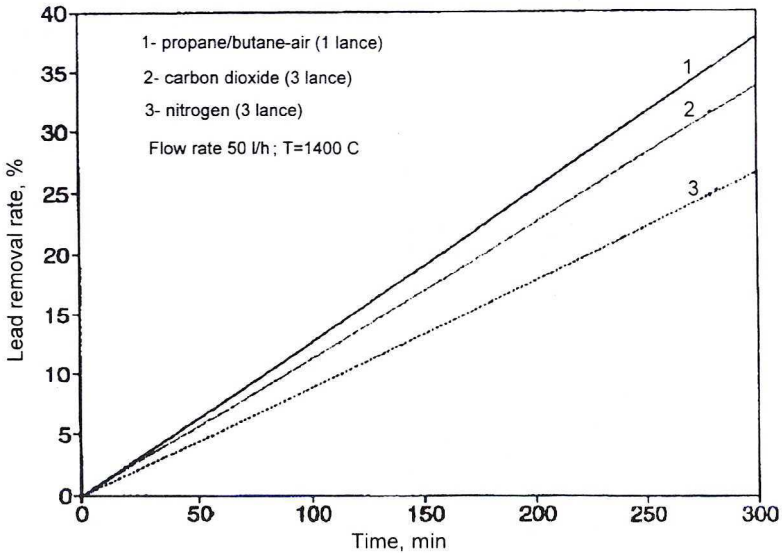


Fig. 6. Relations between the lead removal coefficient from Cu-Pb-Fe alloys and time at 1400°C for various blast gases

The experimental results confirmed quantitatively thermodynamic considerations.

The lead removal depends very heavily on temperature of the alloy and the oxygen pressure of the passing gas. The rate of lead removal from Cu–Pb–Fe alloys increases with the increase of the gas/metal interface. The highest rate of the lead removal from Cu–Pb–Fe alloys was observed during experiment in which air-propane/butane mixture was injected. This phenomenon could be explained by higher oxygen pressure in the bubbles, as well as higher temperature, which could be elevated above furnace temperature as a result of quasi-adiabatic burning of propane/butane gas in the lance and bubbles. In consequence vaporisation of the lead and its oxidation by CO_2 and H_2O , which are products of propane and butane burning would be much faster. In spite of that, no corrosion of the lances was observed.

Utilising the experimental results, amounts of the gases needed to pass through Cu–Pb–Fe alloy in order to remove 1 Mg of the lead were computed. These values are given in table 5. The values are much (several thousands) higher than those estimated from thermodynamic considerations. In plant conditions, the contact between gas and alloy phases should be much longer than during laboratory experiments. However, even in such case, amount of blast gases could be tenth times higher than that computed. It suggests that limiting step in this process is the lead evaporation from Cu–Pb–Fe alloy.

TABLE 5

Amounts of used gases for removal of 1 Mg of lead from Cu–Pb–Fe alloys

Gas	Number of used lances	Temperature, °C	Amount of gas/1 Mg Pb [Nm^3]	Amount of gas/lance/h, [l/h] (in experiments)
Nitrogen	1	1300	171 739	50.0
	3		164 473	8.3
	3	1400	168 918	16.7
	3		49 019	8.3
	3		57 339	16.7
Carbon dioxide	3	1300	68 306	8.3
	3	1400	80 906	16.7
	3		34 435	8.3
	3		50 403	16.7
Propane/butane-air	1	1300	63 938	50.0
	1	1400	31 289	50.0

6. Conclusion

Results confirm thermodynamic considerations. The lead removal rate depends heavily on alloy temperature and oxygen potential of the blast. The rate increases

with the degree of the gas dispersion and hold-up time of bubbles in the melt. It can be concluded from the experimental results that evaporation rate of the lead from Cu-Pb-Fe alloy is a limiting step in this process. The iron from Cu-Pb-Fe alloys was almost completely oxidised in all experiments with oxidising gases. However, no slag on these samples was observed after experiments, hence it is likely that the iron was removed as a dust.

Despite that the results are not encouraging from practical point of view, the direction of the further work which is supposed to lead to solution of the problem is clear. First of all, there is no doubt that temperature of the melt and oxygen potential of the blast gas are the most influential parameters in lead removal process. The influence of such parameters as interface between melt and a gas as well as residence time of the gas bubbles in the melt are also significant, however the possibility to control the process by these parameters are rather limited.

The melt temperature cannot be maintained on too high level, because of lining corrosion rate would be unacceptable. However, the process is still feasible provided that lance design is completely different from those used in the experiments as well as blast contains more oxygen.

REFERENCES

- [1] J. Wypartowicz, Interpretacja własności termodynamicznych ciekłych roztworów w układzie Cu-Pb-Fe-As, Zeszyty Naukowe Politechniki Śląskiej, 48 1995.

REVIEWED BY: PROF. DR HAB. INŻ. JAN WYPARTOWICZ

Received: 5 March 2000.