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Lead removal from brass scrap by fluorine-free compound separation

S. Hilgendorf^{*1,2} , F. Binz¹, J.-M. Welter³ and B. Friedrich¹ 

Taking complexity of process technology, economical and environmental reasons as well as time impact into account, removal of lead based on intermetallics formation and subsequent separation proves to be the most balanced approach. The hitherto used aggregation agent sodium fluoride does serve as a suitable additive in European countries. Therefore, fluorine-free compound separation is evaluated. Thermochemical modelling of Cu–Zn–Pb–Ca–O system identifies ideal process conditions, namely, charging calcium with an amount of 1.5 wt-% at 930°C. Experiments carried out at stated parameters reveal comprehensive formation of Pb–Ca compounds, chemically similar to the stoichiometric intermetallic phase Ca_5Pb_3 . Thus, the results prove the technological feasibility of lead removal from molten brass scrap using fluorine-free compound separation.

Keywords: Lead separation, Brass scrap recycling, Intermetallic compound formation

This paper is part of a Themed Issue on Brass Alloys.

Introduction

Brass alloys offer a unique combination of material strength, corrosion resistance, machinability and formability. Therefore, different types of brasses have a wide range of applications reaching from simple screws and pipes to electrical parts. Although all brass alloys show good machinability compared to other materials, lead is often used as an alloying element to further improve machinability and wear resistance. Lead contents in these brasses can reach up to 4.0 wt-%.¹ As lead is considered a hazardous material due to its neurotoxic effects and impact on fertility, regulations regarding lead have been getting stricter in the last few years. European-based REACH programme will limit Pb-content to 0.5 wt-% ‘in articles supplied to the general public’ comprising brass alloys from June 2016.² In the USA, lead contents in water bearing materials has been limited to 0.25 wt-% since 2014 by the *Safe Drinking Water Act*.³ While producers dealing with primary materials can address this circumstance relatively easy by using lead-free virgin materials, brass rod mills and foundries have to react to these requirements within a short time frame in an environment of sharper public perception. Owing to the significant contribution of brass recycling to environmental and economical sustainability an innovative scientific concept for complex lead separation from brass has to be developed.

Lead control strategies

Most of the well-known metallurgical processes such as selective oxidation and liquation are not applicable in this system due to thermochemical boundaries. A global literature review on practically applicable Pb-elimination methods from brass scrap reveals several approaches. Results are presented below. Note that only processes are reviewed while properties of lead-free brass alloys do not play a role in this section.

Electrolytic decomposing

Electrolytic decomposing marks the only hydrometallurgical approach in this review. German-based copper producer *Wieland-Werke* patented the process in 2011.⁴ It is based on a Cu-refining electrolysis. Cu-bearing electrolyte then is used to leach Cu-bearing flue dusts. Solids are separated to discharge Pb-bearing impurities. The solution is fed to Cu-winning electrolysis before remaining electrolyte is cleaned again and fed into zinc electrolysis. A whole process flowsheet is as shown in Fig. 1. Main products are copper and zinc cathodes (>99.5 wt-% purity) plus Pb-bearing anode sludge.⁴

Pyrometallurgical decomposing

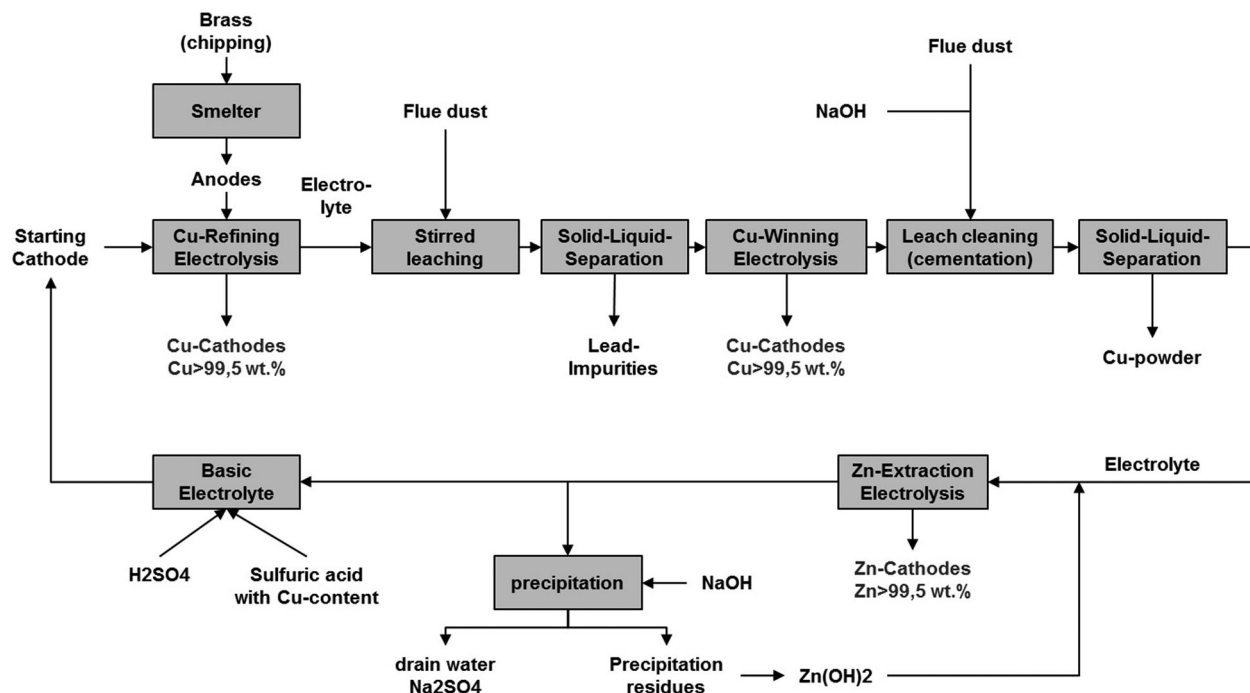
Besides hydrometallurgical decomposing, it is possible to separate leaded brass into its components by consecutive pyrometallurgical processes. At first vacuum distillation is carried out, followed by converting of remaining copper–lead alloy. Both batch processes have been performed in extractive metallurgy for a protracted period, e.g. dezincing of lead,⁵ magnesium production,⁶ converting of copper⁷ and iron.⁸ Therefore, an implementation of this technology should be convenient for leaded brass.

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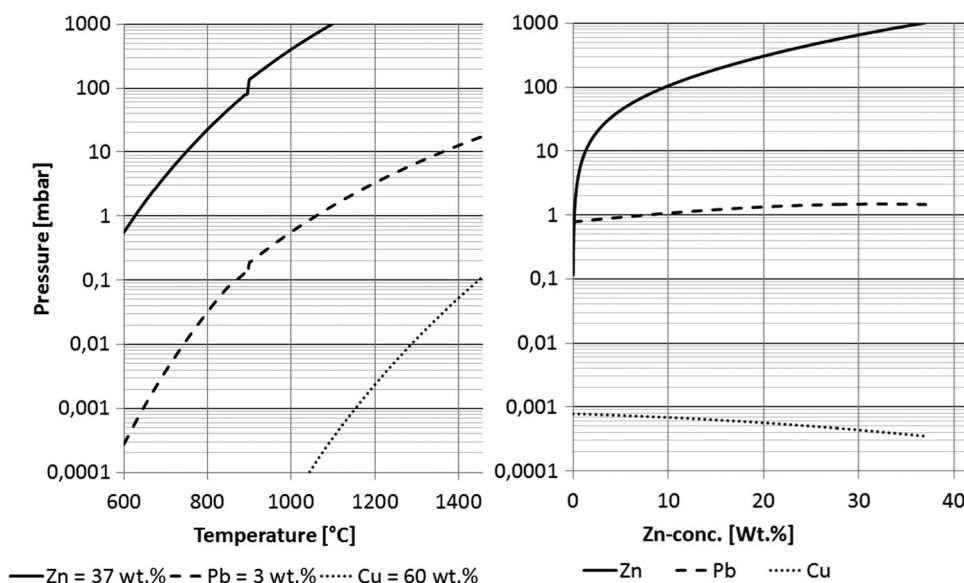


1 Electrolytic separation method for brass-bearing scraps patented by Wieland-Werke⁴

Relatively high vapour pressure of zinc compared to copper and lead enables to volatilise zinc selectively from molten brass. Owing to its chemical activity dependence, the vapour pressure of components in solutions decreases as the concentration falls.⁹ However, considering activities, zinc volatilisation from brass is still possible. Figure 2 shows activity adjusted vapour pressure curves for zinc, lead and copper in CuZn37Pb3, respectively. The modelling done with the thermochemical software *FactSage*TM 6.4 indicates that the vapour pressure of zinc exceeds the ones of both lead and copper by orders of magnitude. More precisely, at liquidus temperature of CuZn37Pb3 (899°C) zinc has a vapour pressure which is approximately 700 times higher than the one of lead

and $7 \cdot 10^7$ higher than the one of copper. The calculations also reveal that the vapour pressures of lead and copper do not – in contrast to zinc – react sensitively to changes in zinc content in the ternary mixture. When the zinc content drops from 37 to 0.1 wt-% at 1100°C the zinc vapour pressure is reduced to 0.8 mbar and thereby equals the corresponding value of lead. Consequently, for targeted zinc levels of less than 0.1 wt-% lead evaporates stronger than zinc because the vapour pressure of lead exceeds the one of zinc.¹⁰

Once zinc is evaporated, molten copper alloy can be further refined by selectively oxidising remaining lead. Taking equilibrium constant (K) dependency into account, Gibbs free energy change of reaction per mole



2 Activity considered vapour pressures of Zn, Pb and Cu as a function of temperature in CuZn37Pb3 alloy (left) and as an isothermal function of zinc content in ternary liquid solution phase at 1100°C (right). Data taken from *FactSage*TM and Nesmejanov¹⁰

oxygen ($\Delta_r G$) is calculated as a function of temperature (T) using the following equation

$$\Delta_r G = \Delta_r G^0 + RT \ln K \quad (1)$$

where R is the ideal gas constant and $\Delta_r G^0$ is the Gibbs free energy of reaction in standard state ($K = 1$). Data for $\Delta_r G^0$ have been obtained from *FactSage*TM. The equilibrium constant for a general oxidation reaction of a divalent metal (Me)



Can be calculated by

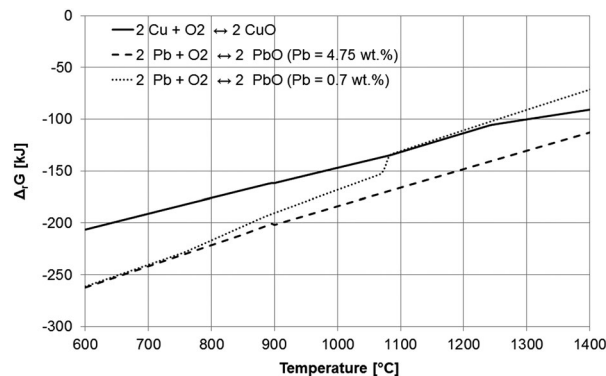
$$K = \prod_i a_i^{v_i} = \frac{a_{\text{MeO}}^2}{a_{\text{Me}}^2 a_{\text{O}_2}} \quad (3)$$

where a_i is the activity of component i and v_i its stoichiometric coefficient. The following calculations are carried out for ideal conditions regarding the activity of metal oxide as well as oxygen ($a_{\text{O}_2} = a_{\text{MeO}} = 1$). Hence, Gibbs free energy of change can be determined by applying this assumption in equation (1)

$$\Delta_r G = \Delta_r G^0 + RT \ln \frac{1}{a_{\text{Me}}^2} \quad (4)$$

Activities for copper and lead are calculated as a function of temperature with *FactSage*TM for concentrations after vacuum distillation, meaning 0.05 wt-% Zn, 4.75 wt-% Pb and 95.2 wt-% Cu. Owing to its strong dependency on the binary composition, Cu–Pb a second calculation for lead considering best possible concentrations for selective oxidation treatment is performed. As Gibbs free energy of copper does not change significantly with changing concentrations only one copper graph is mapped. According to calculation results (see Fig. 3), from a thermodynamic point of view it is not possible to oxidise lead below a target concentration of 0.7 wt-% as Gibbs free energy of reaction for both copper and lead oxidation are almost identical at process temperatures between 1100 and 1200°C.

Experiments analysing vacuum distillation of leaded brass are carried out at IME Process Metallurgy and Metal Recycling using lab-scale medium-frequency induction furnace or rather pilot scale low-frequency induction furnace. Vacuum distillation takes place at



3 Activity corrected Gibbs free energy change of oxidation reaction ($\Delta_r G$) for copper and lead in CuPb4.75 and CuPb0.7 alloy as a function of temperature. Data taken from *FactSage*TM

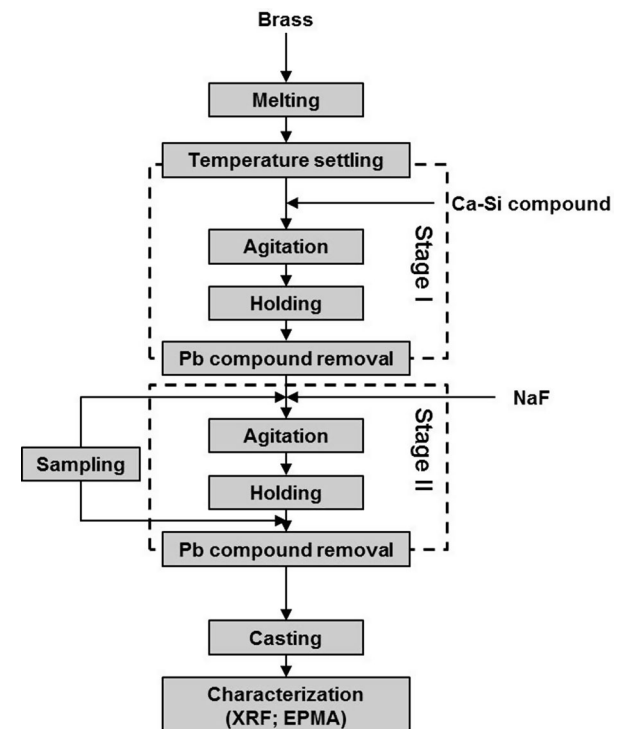
Table 1 Intermetallics densities and melting points in the Ca–Pb System¹⁵

Compound	Ca ₂ Pb	Ca ₅ Pb ₃	CaPb	CaPb ₃
Melting point (°C)	1196	1160	968	666
Density (g cm ⁻³)	4.8	5.1	6.8	9.1

950–1100°C and 1 mbar external pressure. Via liquid condensing metallic condensate containing up to 96 wt-% Zn can be produced. Copper content in obtained ingot is about 99.5%. With the addition of FeO and SiO₂ low-melting Pb-containing fayalite-based slag is generated which can be further refined in order to gain proper material for construction.¹¹

Compound formation and physical separation

A detailed report on lead removal by intermetallics formation from brass was first published by Yamada *et al.*¹² and further developed by Nakano *et al.*¹³ The authors introduced a Ca–Si master alloy into a CuZn39Pb2 alloy to form Ca–Pb intermetallics, which are stable at the process temperature of 910°C. Named stable intermetallics (Table 1) have a density lower and – apart from CaPb₃ – a melting point higher than the liquidus temperature of high zinc brass. They rise to the surface forming a slag which can be skimmed. However, trials showed that formed particles do not necessarily coalesce and smaller particles (<20 µm) do not rise to the surface. Therefore, lead removal rates are not higher than 53%. To increase lead removal the authors added NaF as surfactant and such aggregation agent which increased lead removal rates to 83%, but the exact mechanism



4 Process flowsheet for compound separation of Pb from brass alloys as used by Nakano *et al.*¹³

of NaF is not explained by the authors. Complete flow sheet is as shown in Fig. 4. Published results have been confirmed by Daechang (South Korea) in a series of trials.¹⁴

Dilution

The simplest and cheapest strategy for the rod mills is dilution. It suffices to replenish the home and new scrap with copper and zinc. With some five to 10 dilution cycles the lead content can be brought down to 0.1 wt-%. Considering the short return times, a lead-free rod production can easily be achieved within less than 5 years. Nevertheless, further socio-economical factors have to be considered besides this purely production-based estimate. The learning curve for the use of lead-free brass for small-screw machining shops (as they represent the bulk of the brass machining sector in Europe), the renewing of equipment and forging dies and the necessity to stabilise the market between two dilution cycles in order to avoid a chaotic alloy situation make that a more realistic time span lies between 15 and 25 years.

The fundamental problem is the inflowing old scrap which for a long period of time will strongly limit the yield of dilution. Thus, at first technologies have to be identified which will be able to remove lead from large quantities of old scrap each year in Europe. No precise data exist and an interrogation of the major brass mills only allows an estimation: the quantities should range between 100 000 and 200 000 tonnes.

Comparison of strategies

All presented strategies show different advantages and disadvantages. Therefore, it is hard to give distinct advice to brass mills. Note that the following rating is based on regulations and standards (e.g. health and safety) of European nations as lead removal is addressed by these.

A comparison of strengths and weaknesses under the assumption that sustainability, impact time as well as health and safety are the most essential criteria concludes that three strategies stand out. These strategies are dilution, pyrometallurgical decomposing and compound separation. Possibly a mixed approach depending on the general availability of brass scrap has to be chosen. An important criterion will also be the time span allowed by the regulators.

Dilution needs neither specific equipment nor new know-how and there is no loss in metal value. Its inconvenience is a somewhat longer intrinsic execution period. Pyrometallurgical decomposition based on vacuum distillation and subsequent converting is widely known and applicable to leaded brass. Although it is rated positive in nearly all categories, process technology is challenging and brass mills might be reluctant to introduce it. Second promising strategy under named assumptions is compound separation as no additional infrastructure is needed and nearly all other criteria are rated positive. Health and safety marks the only exception besides environmental concerns as NaF is used in the process. If a NaF-free similar process based on compound separation is developed, this might be the most applicable solution.

Understanding the formation mechanism of Ca–Pb compounds in brass melts

As mentioned above a lead removal process from brass based on lead–calcium intermetallics formation without the use of NaF has not been developed yet. To achieve this goal IME is working on development of such process in close contact with industry. This scientific approach modifies Kosaku's concept of introducing calcium in molten brass. Instead of using fluorine compounds the separation of Ca–Pb intermetallics is carried out by buoyancy force only. A more detailed comprehension of the formation mechanism is necessary in order to effectively remove lead from brass. In a first effort, fundamental research was carried out by thermochemical modelling and physical trials.

Thermochemical modelling of compound formation

Thermochemical modelling was carried out using simulation software *FactSage*TM 6.4. The modelling step followed different aims regarding the Cu–Zn–Pb–Ca–O system:

- Principle effect of variable Ca-addition
- Derivation of optimal process parameters regarding Ca-addition and temperature from these calculations

For all modelling approaches, if not stated different, a CuZn37Pb3 alloy is used as a base. All datasets are taken from unmodified *FactSage*TM databases. *FScope* database is required for the modelling of all liquid and solid solutions as well as Cu-containing intermetallics. *FSlead* is used as a source for Pb–Ca intermetallics thermochemical data. *SGPS* provides data on more possible intermetallics (especially Ca–Zn system). As *FScope* and *FSlead* contain data for a few identical phases, correct calculation requires to exclude duplicates. Solution models needed are all solid and liquid solutions from *FScope*. Even if some of the phases will not appear (e.g. γ solution) their possible existence should be taken into account.

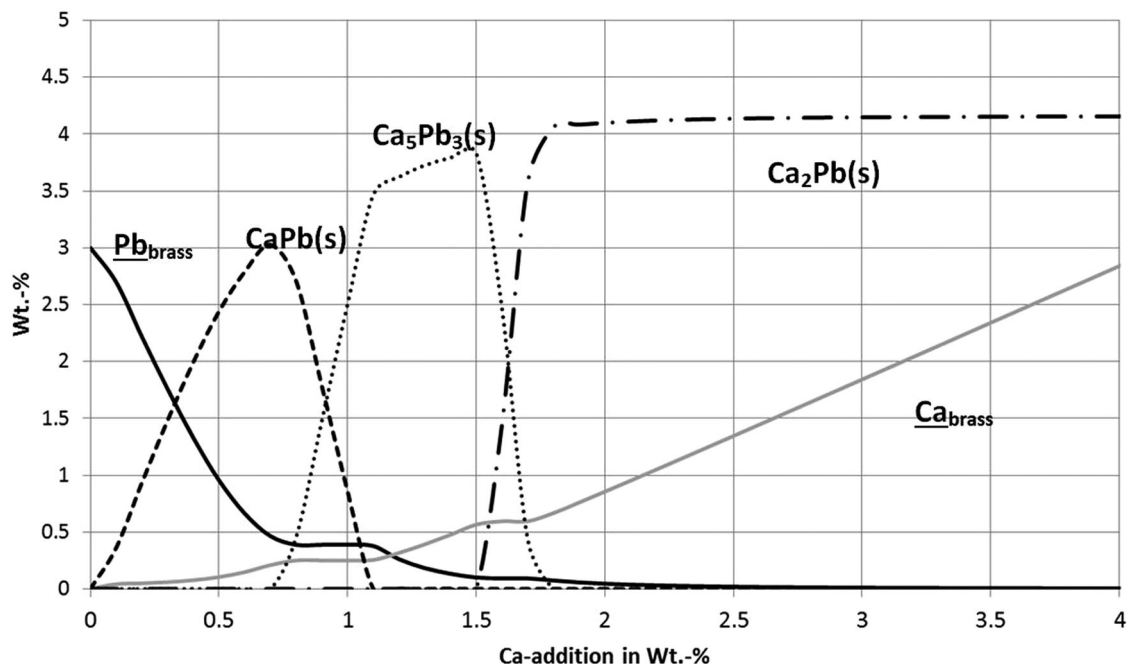
Effect of Ca-addition at a given temperature

In a first step, Ca-addition effect at a given temperature is simulated to understand formation order of intermetallics and reveal possible Zn and Cu losses. Results of the thermochemical calculation for a temperature of 910°C are as displayed in Fig. 5.

Different Pb-bearing intermetallics form in the order $\text{CaPb} \rightarrow \text{Ca}_5\text{Pb}_3 \rightarrow \text{Ca}_2\text{Pb}$ with increasing Ca/Pb ratio. While dissolved Pb is reduced to <0.05 wt-% at Ca-addition of 2.0 wt-% further Ca-addition does not promote effective intermetallics formation due to lower activity of dissolved lead. Excess Ca is dissolved in the liquid brass phase without formation of solid Ca–Zn or Ca–Cu phases. Modelling shows that a CaZn intermetallic phase is stable at temperatures <810°C if excess calcium is available: This phase is not likely to be observed in actual melts as diffusion in the solid phase is hindered.

Derivation of optimal temperature and Ca-addition

Formation of intermetallic phases is modelled for a temperature range of 900–1100°C in 10°C intervals. For every



5 Influence of Ca-addition onto lead content of a CuZn37Pb3 at 900°C.

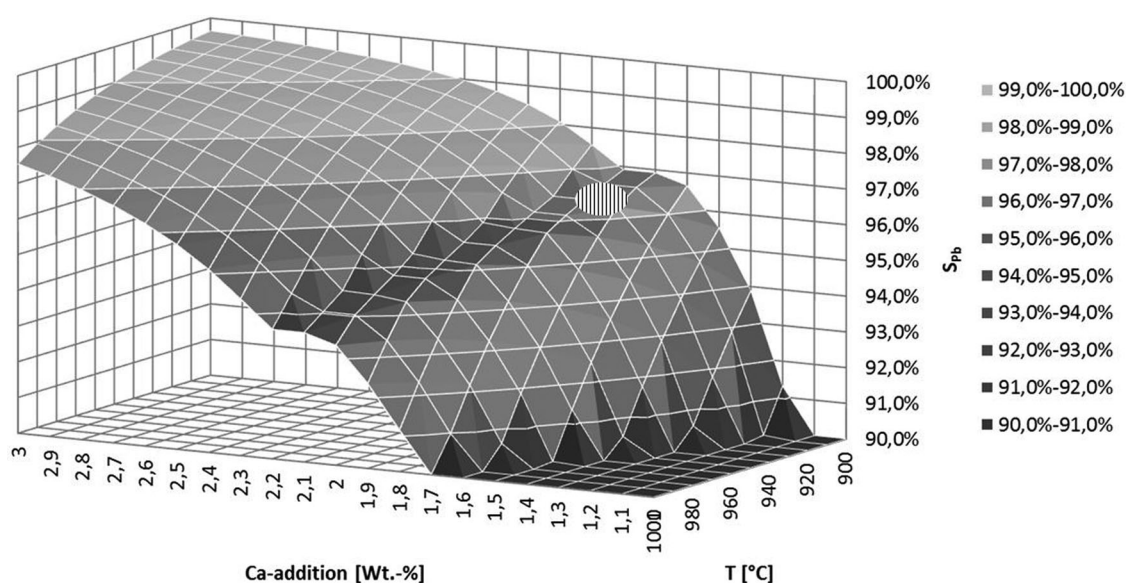
temperature melt composition as function of Ca-addition of 0 to 3 wt.-% in 0.1 wt.-% intervals is calculated. The large amount of data is combined into a model which gives lead separation efficiency as function of temperature and Calcium addition under the assumption that all solid Pb–Ca intermetallics rise to the surface and can be skimmed. Pb-separation efficiency is calculated by equation

$$s_{Pb} = \frac{m_{Pb}(T, Ca)}{m_{Pb0}} \quad (5)$$

where s_{Pb} is the lead separation efficiency and m_{Pb} is the dissolved mass of Pb in brass at a given combination of variables compared to the initial amount of dissolved

lead in brass. Figure 6 shows result of the calculation in the temperature range from 900 to 1000°C and Ca-additions from 1.0 to 3.0 wt.-%. Effect of rising temperature on Ca-effectivity is negative as Ca-tends to dissolve in the brass at higher temperatures. Temperatures lower than 900°C are meaningless due to solidification of the melt. Pb-separation increases with Ca-addition while the dent in the shown diagram is caused by the transition $Ca_5Pb_3 \rightarrow Ca_2Pb$.

Desirable process parameters are 930°C as compromise between Ca-effectivity and melt viscosity. Ca-addition should be 1.5 wt.-%. Under these conditions lead removal rates of 97% are achievable in theory. Higher Ca-additions are not feasible as Ca-effectiveness decreases at additions >1.5 wt.-%.



6 Dependency of Pb-separation efficiency (s_{Pb}) from CuZn37Pb3 at variable temperature and Ca-addition with favourable working domain

Table 2 Composition of brass before Ca-treatment analysed by AES

Cu/wt-%	Zn/wt-%	Pb/wt-%	Sn/wt-%	Ni/wt-%	Bi/wt-%
57.71	39.07	2.89	0.17	0.06	0.01

Experimental validation of phase formation and separation

Based on results from thermochemical modelling, experiments analysing NaF-free lead removal by lead–calcium intermetallics formation are carried out at *IME*. Industrial brass production scrap kindly supplied by *KME Germany* (see Table 2) is used in all trials. In order to achieve a lead content of ~3 wt-% in CuZn39Pb3 alloy, soft lead is added before calcium treatment. Calcium is introduced into molten brass at temperatures between 930 and 950°C by using calcium cored copper wire kindly provided by *Affival*. Temperature monitoring is realised via type-K thermocouple which requires using SiC protection tube. Temperature measurement accuracy is within $\pm 3^\circ\text{C}$.

For all lab scale trials, 7.5 kg of brass scrap is charged and subsequently melted in a medium frequency induction furnace before adding calcium. These experiments are designed to get a first evaluation of lead removal rates by calcium cored wire addition without using sodium fluoride. Large scale trials with an input of 150 kg are carried out in a resistance heated furnace. The attached rotary injection stirrer enables to investigate the influence of stirring with or without nitrogen purging on the buoyancy of intermetallics in molten brass. Experimental setup of both lab scale and pilot scale are as shown in Fig. 7.

Results and discussion

Metal samples are analysed using atomic emission spectroscopy (AES) as well as scanning electron microscopy (SEM-EDS). AES results of small-scale trials show poor lead removal rates compared to the use of sodium

fluoride. In a best-case scenario, around 20% of initial lead can be removed by formation and buoyancy-driven separation of intermetallic particles. Nitrogen purging does not significantly influence lead removal rates. More precisely, in pilot scale trials lead removal rates are increased to at best 28% while using nitrogen purging. Table 3 provides a summary of experimental conditions and achieved best-case lead removal rates.

High lead levels after calcium treatment of molten brass without using sodium fluoride leave the question if formation of Pb–Ca intermetallics is successful under given conditions. SEM in backscattered mode of brass samples after calcium treatment reveals white spots which represent the intermetallics in a Cu–Zn matrix (see Fig. 8). The Ca/Pb ratio of 1.5 in this inclusion indicates predominant formation of stoichiometric intermetallic phase Ca_5Pb_3 ($\text{Ca/Pb} = 1.67$) which matches the most stable Pb-bearing compound of thermochemical modelling while adding 1.5 wt-% of calcium (see Fig. 5). This result is evidence for proposed reaction product.

With sizes ranging from sub-micrometric to some 30 μm , the Pb–Ca phase is finely dispersed and can be found all over the samples regardless of the implementation of a purging step. This not only reflects clearly comprehensive formation of Pb–Ca–intermetallics but also insufficient agglomeration behaviour caused by wettability between intermetallics and melt. Apparently, neither buoyancy nor purging leads to suitable sizes of intermetallic inclusions. Therefore, resulting buoyancy forces proportional to the size are small and phase separation hardly takes place. These results are consistent with those published by Nakano *et al.*¹³

Assessment and outlook

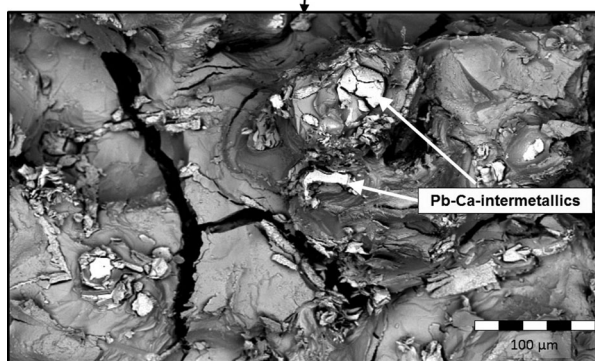
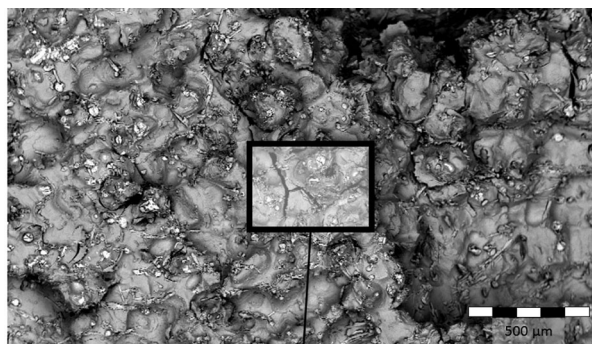
Thermochemical modelling of Cu–Zn–Pb–Ca–O system identifies ideal process conditions in order to achieve highest theoretically reachable lead removal rates, namely charging calcium with an amount of 1.5 wt-% at 930°C. Experiments carried out at stated parameters reveal comprehensive formation of Pb–Ca compounds, chemically similar to stoichiometric intermetallic phase Ca_5Pb_3 . Separation, though, remains problematic. Owing to particle



7 Experimental setup: induction promoted floating with 7.5 kg input (left) and gas promoted floating with 150 kg input (right)

Table 3 Experimental conditions and Pb-separation efficiency

Scale	No. of exp.	Purging used	Input mass/kg	Ca added/wt-%	Addition temp./°C	$s_{Pb}/\%$
Lab	2	No	7.5	1.5/3	930–950	18.4
Pilot	5					21.2
	3	Yes	150	1.5		31.7

**8 SEM images of Pb–Ca intermetallics in brass matrix**

sizes smaller than 30 μm buoyancy forces are rather small. However, these results are based on preliminary experiments. In spite of the fact that the precise mechanism of sodium fluoride remains unknown, it seems to be inevitable to use surfactants in order to achieve high lead removal efficiencies from molten brass via Pb–Ca intermetallics formation. Thus, we can conclude by saying that the key issue of a successful process is not its thermodynamics, but an insufficient kinetics.

Especially effects of boundary layers need further investigations. Furthermore, alternative process design considering phase separation of formed intermetallics from molten brass, e.g. filtration or centrifugation needs to be analysed. This work will be carried out by IME and IWKS in a close collaborative approach with industrial brass mills.

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