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# Mechanism of Pb Removal from Brass Scrap by Compound Separation Using Ca and NaF

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## Abstract

The Mechanism of Pb removal from brass scrap by compound separation using Ca and NaF addition was investigated. Because large Ca-Pb compound particles formed by Ca addition rise to the surface of the molten brass, they can be skimmed off from the molten brass. However, fine Ca-Pb compound particles remain in the molten brass because of low buoyancy. By subsequent NaF addition, the reaction between Ca-Pb compound and NaF takes place at their contact regions, resulting in the formation of solid $CaF_2$, liquid Pb and Na gas. Pb is mainly present at the Ca-Pb compound-$CaF_2$ interface. $CaF_2$ acts as a binder for aggregation of fine Ca-Pb compound particles, resulting in the formation of light and large composite compounds, which rise to the surface of the molten brass. A high Pb removal rate is achieved by skimming off.

## Keywords

Lead Removal, Brass Scrap, Calcium, Sodium Fluoride, Compound Separation

## 1. Introduction

The machinability of brass alloys containing Pb is better than those of other metallic materials. However, Pb is a harmful substance that has neurotoxic effects and affects fertility. In Japan, the permitted level leached Pb in drinking water supplies was revised to 0.01 mg/L in April 2003 [1]. In European-based REACH program, the limit Pb content in brass alloys has been decreased 0.5 wt % from June 2016 [2]. In the USA, the Pb content in water-bearing materials has been limited to 0.25 wt % since 2014 [3].

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Brass alloys are mainly manufactured by recycling brass alloy scrap. The simplest strategy for Pb reduction is dilution using Pb-free virgin materials. This method is used widely at present at most brass mills. However, the fundamental and troublesome problem is the accumulation of large amounts of unrecycled scrap. This confuses the recycling system functioning at present. The development of new technology for removing Pb from brass alloy scrap is urgent. For a hydrometallurgical approach, electrolytic decomposing in which main products were Cu and Zn cathodes plus Pb-bearing anode sludge was patented in 2012 [4]. Besides hydrometallurgical decomposing, pyrometallurgical decomposing based on vacuum distillation and subsequent converting of remaining leaded brass is widely known and applicable to leaded brass [5]. However, large additional infrastructure is needed at most brass mills. Compound separation method is the most practical method because no additional infrastructure is needed [5]. A method for Pb removal by compound separation using Ca-Si compound and NaF addition was first reported by the authors *et al.* [6] [7]. Hilgendorf *et al.* reported a fluorine-free method involving Ca addition alone [5]. However, there are few reports about Pb removal using compound separation.

According to the results reported as yet [5] [6] [7], the Pb removal rate was about 20% in the case of Ca-Si compound or Ca addition alone and increased to 83% on subsequent NaF addition. However, the reasons for the effect of NaF on Pb removal have not been elucidated. Clarification of this removal mechanism would enable the development of methods for Pb removal by Ca and NaF additions and for fluorine-free Pb removal. This mechanism was therefore investigated in the present study.

## 2. Experimental

Brass scrap (chemical composition: 59.6 wt % Cu, 3.2 wt % Pb, 0.3 wt % Sn, 0.16 wt % Fe, 0.05 wt % Ni, bal. Zn, ingot weight: 10 kg) was charged and then melted in a graphite crucible of 165 mm outer diameter, 139 mm inner diameter and 210 mm height (Nippon Crucible, Tokyo, Japan) in a high-frequency (6 - 9 kHz) induction furnace (MELT-COMP-80K, Tamagawa Engineering, Fukushima, Japan) in the atmosphere. The temperature was monitored with an inset type of optical fibre pyrometer (FIMTHERM-HM, Seiyo Industry, Yokohama, Japan). A Ca-cored brass wire of 13.6 mm outer diameter and 12.8 mm inner diameter (WING ON, Tokyo, Japan) was added to the molten brass at 1193 K, followed by manual agitation for 1 min and holding for 5 min. The addition amount of Ca was 2 wt %. The temperature of the molten brass rose to 1223 K because of an exothermic reaction. After skimming off the floating slag using a ladle, a small sample disk of 40 mm diameter and 25 mm height for chemical analysis was produced by partial casting using the ladle and metal molds. NaF (Showa Chemical, Tokyo, Japan) of 4 wt % was then added to the molten brass at 1223 K, followed by manual agitation for 1 min and holding for 5 min. The slag and a small sample disk were similarly collected. The slag was characterized using

scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) (SEM; JSM-7001F, JEOL, Tokyo, Japan, EDS; INCAx-act, Oxford Instruments, Oxfordshire, United Kingdom) and X-ray diffraction (XRD) (Smart Lab 9 kW, Rigaku, Tokyo, Japan) with Cu-Kα radiation. The electric voltage and current applied to the X-ray tube used for XRD were 45 kV and 200 mA, respectively. The scanning rate and step angle were 50˚/min and 0.02˚, respectively. The chemical composition and microstructure of the small sample disk were examined using X-ray fluorescence (Simultix 14, Rigaku, Tokyo, Japan) and SEM-EDS, respectively.

## 3. Results and Discussion

The Pb removal rate after Ca addition was 15%. Figure 1 shows the XRD pattern of the slag after Ca addition. Large amounts of ZnO [8] and small amounts of CuO [8], CaO [9] and $Ca_2PbO_4$ [10] were identified, but no PbO was identified. The standard Gibbs free energies ($\Delta G^\circ$) of the oxidation of Zn, Cu, Pb and Ca at 1223 K were calculated using HSC Chemistry 5 software (Outokumpu Research). The values of $\Delta G^\circ$ for ZnO, CuO, PbO and CaO were −447, −95, −198 and −1012 kJ/mol, respectively. The $\Delta G^\circ$ value of ZnO is lower than those of CuO and PbO. This suggests that ZnO is formed in preference to CuO and PbO in the molten brass. The presence of large amounts of ZnO in the slag is caused by this phenomenon. However, small amounts of CuO also exist in the slag as shown in Figure 1. This is caused by atmospheric oxidation of brass alloy contaminated in the slag during skimming off, which is achieved during air cooling after skimming off. The reaction between Ca and Pb occurs by Ca injection into the molten brass, resulting in the formation of a Ca-Pb compound. The oxidation of Ca also occurs because the $\Delta G^\circ$ value of CaO is lower than that of ZnO. The presence of small amounts of CaO in the slag is caused by this phenomenon.

Figure 2 shows the SEM-EDS results for the small sample disk after Ca addition. Ca and Pb can be detected in the white region in the SE image. This indicates the presence of the Ca-Pb compound in the molten brass. It is known that $Ca_2Pb$ is formed at Ca addition of 2 wt % [5]. The $\Delta G^\circ$ value for the reaction
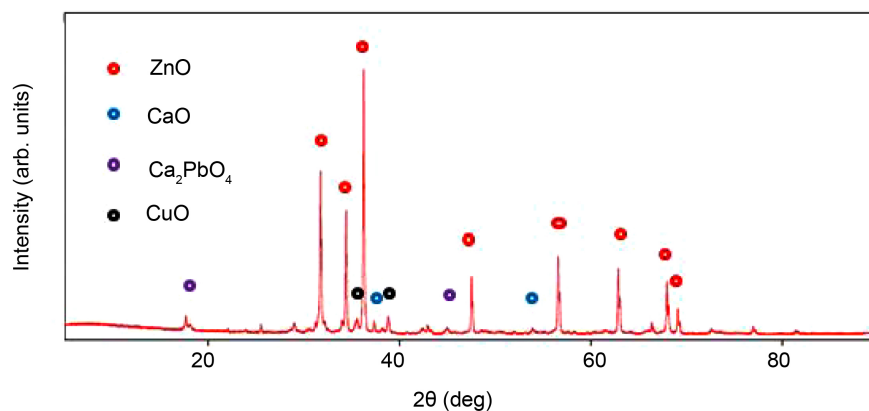


**Figure 1.** XRD pattern of slag after Ca addition.
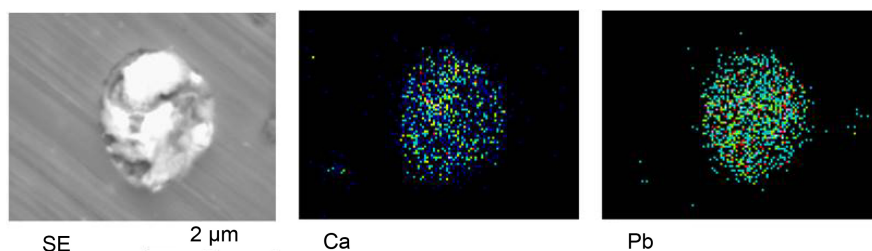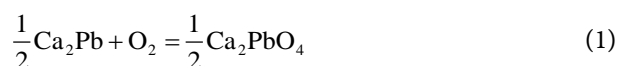
SE    2 μm    Ca    Pb

**Figure 2.** SEM-EDS results for small sample disk after Ca addition.

between the $O_2$ gas in air and $Ca_2Pb$ (Equation (1)) was calculated using HSC Chemistry 5 software.

$$\frac{1}{2}Ca_2Pb + O_2 = \frac{1}{2}Ca_2PbO_4 \tag{1}$$

The value of $\Delta G^{\circ}$ at 1223 K was −425 kJ/mol. This value is negative, therefore the reaction can occur. The results show that $Ca_2Pb$ is formed in the molten brass after Ca addition and then $Ca_2PbO_4$ is formed by atmospheric oxidation of $Ca_2Pb$ during air cooling after skimming off. The large $Ca_2Pb$ particles that rise to the surface of the molten brass can be skimmed off, but fine $Ca_2Pb$ particles remain in the molten brass. A high Pb removal rate therefore cannot be achieved by Ca addition alone.

The Pb removal rate after NaF addition was 72%. The SEM-EDS results for the slag after NaF addition are shown in **Figure 3**. Regions in which Ca, Pb and O coexist ($Ca_2PbO_4$) and Pb and O coexist (PbO) are present. Ca, Na, Zn, F and O are all present in the same region. This suggests that Ca and Na fluorides and Ca and Zn oxides coexist.

**Figure 4** shows the XRD pattern of the slag after NaF addition. NaF [11], ZnO, CaO, $Ca_2PbO_4$, $CaF_2$ [12], and PbO [13] were identified. However, no CuO was identified. This may be caused by few brass alloy contamination in the slag. PbO, as well as $Ca_2PbO_4$, is thought to be formed by atmospheric oxidation of Pb during air cooling after skimming off. This suggests that Pb is present in the molten brass. The presence of Pb is caused by the decomposition of $Ca_2Pb$. Similarly, the presence of $Ca_2PbO_4$ in the slag indicates that $Ca_2Pb$ is present in the molten brass. It is considered that most of the $Ca_2Pb$ does not decompose in the molten brass and remains unchanged. This suggests that the $Ca_2Pb$-NaF reaction occurs mainly at their contact region.

The $\Delta G^{\circ}$ values for the reaction between NaF and $Ca_2Pb$ (Equation (2)) and NaF and excess Ca not involved in the Ca-Pb reaction (Equation (3)) were calculated using HSC Chemistry 5 software.

$$\frac{1}{4}Ca_2Pb + NaF = \frac{1}{2}CaF_2 + \frac{1}{4}Pb + Na \tag{2}$$

$$\frac{1}{2}Ca + NaF = \frac{1}{2}CaF_2 + Na \tag{3}$$
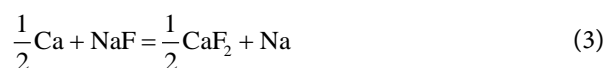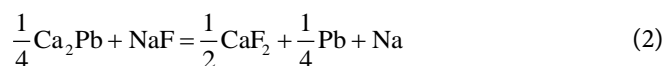
The values of $\Delta G^{\circ}$ for reactions (2) and (3) at 1223 K were −26.8 and −62.4
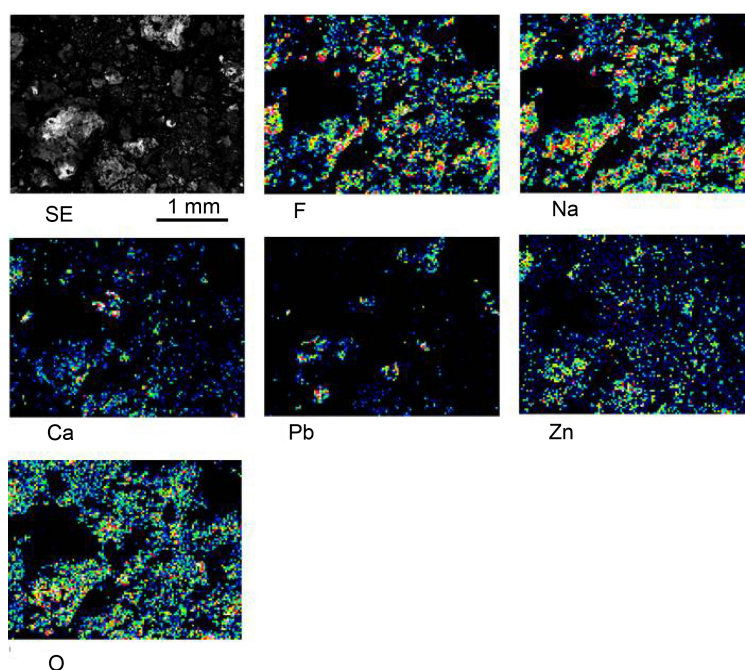
4

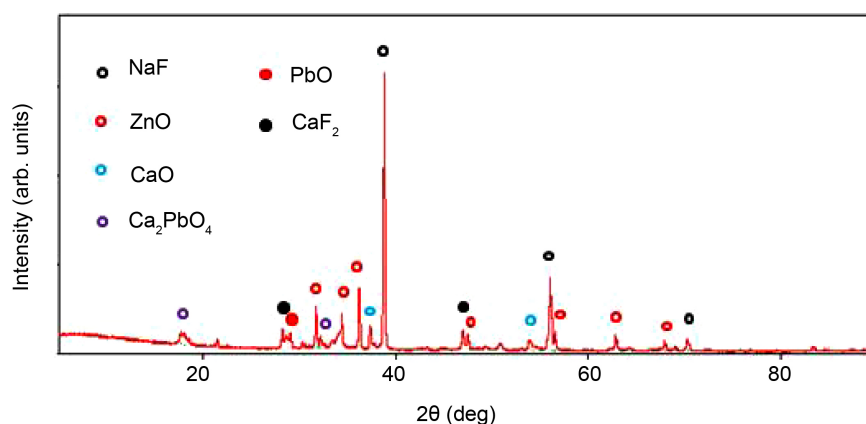**Figure 3.** SEM-EDS results for slag after NaF addition.



**Figure 4.** XRD pattern of slag after NaF addition.

kJ/mol, respectively. Because both values are negative, these reactions can occur. The value for reaction (3) is lower than that for reaction (2). Therefore, reaction (3) occurs preferentially until the excess Ca is almost all consumed, and then reaction (2) occurs.

In the molten brass at 1223 K, $Ca_2Pb$ and $CaF_2$ are solid because the melting points of $Ca_2Pb$ and $CaF_2$ are 1469 and 1691 K, respectively [14]. The melting point of NaF is 1266 K. Therefore, NaF is present in solid form. Pb which has a low melting point (600 K) is present as a liquid. Na becomes a gas because of its low vaporization temperature (1156 K).

A schematic illustration of the mechanism of Pb removal based on the above results is shown in **Figure 5**. On NaF addition, the reaction (2) occurs at the $Ca_2Pb$-NaFcontact region, resulting in the formation of $CaF_2$ (solid), Pb (liquid),
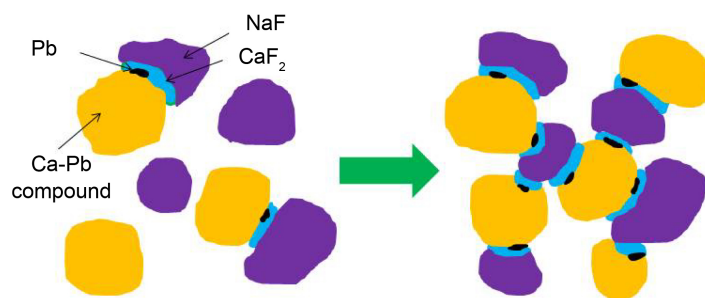
**Figure 5.** Schematic illustration of mechanism of Pb removal using Ca and NaF addition.

and Na (gas). It is considered that Pb is mainly present at the $Ca_2Pb$-$CaF_2$ interface. Na gas is released from the molten brass. By agitating after NaF addition, multiple aggregation of residual fine $Ca_2Pb$ particles is promoted by $Ca_2Pb$-$CaF_2$-NaF joining, resulting in the formation of large composite compounds. Thus, $CaF_2$ acts as a binder for aggregation of fine $Ca_2Pb$ particles. The densities of these large composite compounds are low because the densities of NaF (2.79 $g/cm^3$) and $CaF_2$ (3.18 $g/cm^3$) are lower than that of $Ca_2Pb$ (4.8 $g/cm^3$) [14]. These light and large composite compounds rise to the surface of the molten brass because of high buoyancy. A high Pb removal rate is achieved by skimming off.

In the case of Pb removal by Ca addition alone, excess Ca causes new and complicated problems such as precipitation of Ca-Zn intermetallic compounds during solidification [5]. However, this problem can be solved because the excess Ca is nearly all consumed by NaF addition (reaction (3)).

## 4. Conclusion

In the case of Ca addition alone, fine $Ca_2Pb$ particles remain in the molten brass because of low buoyancy. Subsequent NaF addition leads to $CaF_2$ formation by a reaction occurring at the $Ca_2Pb$-NaF contact region. Large composite compounds are formed by multiple aggregation of residual fine $Ca_2Pb$ particles because $CaF_2$ acts as a binder between $Ca_2Pb$ and NaF. These light and large composite compounds rise easily to the surface of the molten brass, enabling Pb separation by skimming off. A high Pb removal rate is therefore achieved. Thus, the key issues of a successful process are thermodynamics and kinetics of compound particles. In particular, the relationship between additive and buoyancy needs further investigations.

## Acknowledgements

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