



Penetration analysis of elements and bioleaching treatment of spent refractory for recycling

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Abstract

Acidithiobacillus ferrooxidans ATCC23270 and *Acidithiobacillus thiooxidans* TM-32 were used for bioleaching of spent refractories of aluminium and copper melting furnaces for their recycling. Firstly, penetration of elements into aluminium melting furnace refractory was investigated and it was found that up to 7 cm from surface was contaminated. Comparison on leaching efficiency by the strains ATCC23270 and TM-32 found that the strain ATCC23270 could treat larger amount of the refractories than the strain TM-32 could do. In the experiment of bioleaching of spent refractory aluminium melting furnace by the strain ATCC23270, high leaching efficiency were obtained on Al, Si, and Ca, and extremely low leaching performance was, however, shown on the rest of elements i.e., Na, Mn, and Zn. Under the strain TM-32 use, relatively high leaching performance was recognized on Al, Si, Ca, Na, Mn, and Zn. In the experiment of bioleaching for spent refractory copper melting furnace, almost the same leaching trends were shown on Cu, Zn, Al, and Si under the strains ATCC23270 and TM-32 uses.

Key words: spent refractory; penetration of elements; bioleaching; recycling

Introduction

Refractory is the internal lining materials for incinerators and melting furnaces. It is an essential material for those vessels to have heat resistant and should be replaced regularly due to fatigue and damage of refractory caused from operation during its service period. Approximately three million metric tons of refractory were in use by industries in USA (Bennett and Kwong, 1997) and 80000 metric tons of spent refractory was generated in European Union (EU) (Ortega, 1998). Most of spent refractory was used to be directly dumped into landfill sites with and without intermediate treatment (Maginnis and Bennette, 1995; Bennett and Kwong, 1997; Fang, 1999), which accelerates the end of life of a landfill site that is extremely difficult to be newly built in Japan. Recently, recycling of spent refractory has been recognized by industries, for examples, 18% of spent refractory in the EU is landfilled (Bennett and Kwong, 2004) and some industries such as glass and steel in France have shown 90% of recovery level of spent refractory (Ortega, 1998). Spent refractory is recycled into the following applications; refractory component, insulating powder, carbon and silicon source, soil conditioner, abrasive, and so on (Bennett and Kwong, 2004), however, the recycling of refractory heavily depends on economic condition of companies not on recycleability of refractory (Bennett and Kwong, 2004). For recycling

of refractory, contamination of refractory by hazardous organic compounds such as dioxins and by unwanted elements such as heavy metals and any elements with high accumulation is one of obstacles. Contamination by unwanted elements leads to more problems than that by the organic compounds, as organic compounds can be degraded to harmless products like carbon dioxide, water, and HCl, heavy metals can only be mobilized or immobilized. Heavy metals stay forever unless they are removed from contaminated refractory. Recycling concept is shown in Fig.1. When spent refractory is generated, penetration depth of refractory contamination by hazardous organic compounds and the unwanted elements is predicted using the universal equation which is under development by the author. Knowing the level of contamination in refractory by unwanted elements is important for recycling of spent refractory in order to remove contaminants. Once contamination depth is known, the refractory lies within contaminated depth is scraped and collected for following intermediate treatment. The uncontaminated refractory directly is sent to recycling process.

In this study, spent refractories of aluminium and copper melting furnaces were treated by bioleaching to assure leachability of unwanted elements from refractories by microbes. Firstly, penetration of elements into the refractory was investigated by instrumental analysis. Bioleaching was applied for treatment of contaminated refractory. Since Tateda *et al.* (1998) and Ishigaki *et al.* (2005) employed

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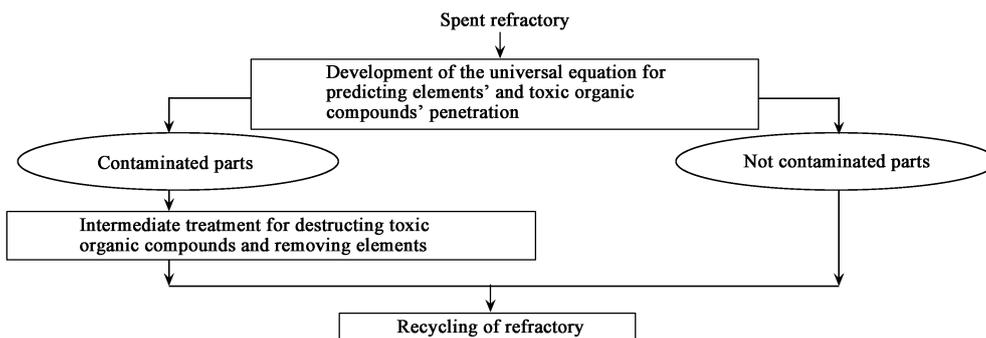


Fig. 1 Recycling concept of refractory.

bioleaching technology for extracting contaminants and recovering valuable metals from fly ash of municipal solid waste incineration ash and they concluded that the technology was a very useful and a promised process for element recovery, the same technology was applied to spent refractory treatment. Iron and sulfur oxidizing bacteria were employed and bioleaching characteristics of the refractories were discussed. This is the first report on application of bioleaching to spent refractories.

1 Materials and methods

1.1 Refractory

Sampling of spent refractory of aluminium melting furnace was obtained at the aluminium processing factory in Toyama, Japan. Sampling spots are shown in Fig.2 and samples at the three spots in the aluminium melting furnace were collected. Sampling spot A was the bed of the opening mouth of the furnace where waste aluminium products such as waste window frames and waste wheels for cars were thrown in. The spot B was a lower part of the side wall below the level of melting aluminium. The spot C was an upper part of the side wall near the ceiling. Spent refractory of copper melting furnaces was also obtained from the copper processing process in the same factory where spent refractory of aluminium melting furnace was taken and the refractory was sampled at a spot which had been located below the level of molten copper in the furnace. Components of those refractories are shown in Table 1.

Table 1 Composition of refractories of the aluminium and copper melting furnaces

Component	Aluminium (%)	Copper (%)
Al ₂ O ₃	83	34
SiO ₂	11	22
Others (Fe, Ti, Ca, Mg, Na, K,...)	6	44

1.2 Strains and media

Acidithiobacillus ferrooxidans ATCC23270, an iron oxidizing bacterium, and *Acidithiobacillus thiooxidans* TM-32, a sulfur oxidizing bacterium, (Tateda *et al.*, 1998; Ishigaki *et al.*, 2005) were used for bioleaching of spent refractories of aluminium and copper melting furnaces. The 9K (KCl 100 mg/L, MgSO₄·7H₂O 500 mg/L, K₂HPO₄ 500 mg/L, (NH₄)₂SO₄ 3.0 g/L, Ca(NO₃)₂·4H₂O 10 mg/L, FeSO₄·7H₂O 44.2 g/L) and ONM (MgSO₄·7H₂O 300 mg/L, KH₂PO₄ 4.0 g/L, (NH₄)₂SO₄ 2.0 g/L, CaCl₂·2H₂O 300 mg/L, elemental sulfur 10 g/L) media were used for the strains ATCC23270 and TM-32, respectively (Chida, 1996). 9K + S medium (9K + elemental sulfur 10 g/L) was used for the mixed culture of the strains ATCC23270 and TM-32.

1.3 Analytical method

Element concentrations were measured by ICP-MS (Agilent 4500, Hewlett Packer, USA). The pH and oxidation-reduction potential (ORP) in cultures at the time intervals were measured by pH electrode #6328-10C (Horiba, Japan) and ORP electrode #6811-06C (Horiba, Japan), respectively.

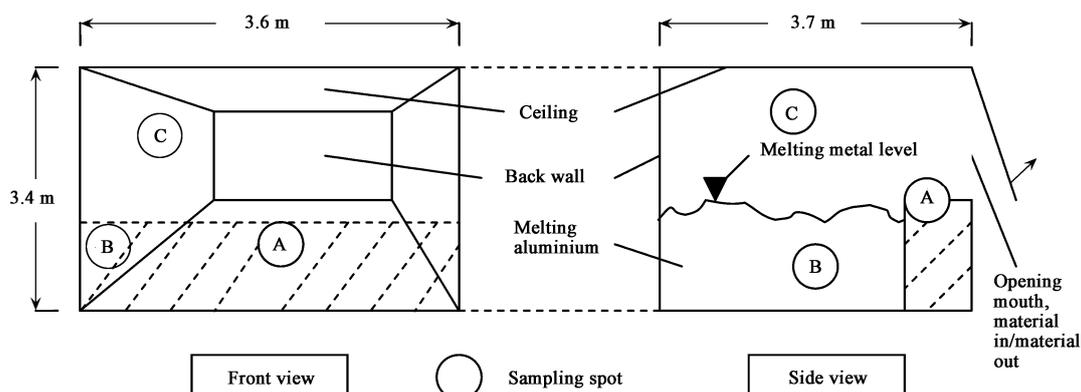


Fig. 2 Sampling spots in the furnace.

1.4 Element penetration analysis

Refractory samples obtained from each sampling spot and the obtained samples were scraped at surface, 1 cm depth, 3 cm depth, 5 cm depth, 7 cm depth, 10 cm depth and 15 cm depth for the sample at each depth (Fig.3). Each sample was, then, placed into two agate grinding bowls (40 ml × 2) and was grinded into under 1 μm by a Planetary Ball Mill P-7 (Fritsch, Germany) at 800 r/min for 10 min. After the process, each fine sample was pretreated with nitric acid and hydrochloric acid by boiling for element analysis following Japan Standard Method (Japan Sewage Works Association, 1997). The experiments were in duplicate or triplicate, and standard deviations were less than 5% (data not shown).

1.5 Bioleaching test

Obtained spent refractories of aluminium and copper melting furnaces were pretreated before bioleaching. Each sample was placed into two agate grinding bowls (40 ml × 2) and was then grinded into under 1 μm by a Planetary Ball Mill P-7 (Fritsch, Germany) at 800 r/min for 10 min. Next, each fine refractory sample was added into 100 ml of 5-d pure cultures and the mixed cultures of the strains ATCC23270 and TM-32 and continuously incubated on a rotary shaker at 120 r/min and 30°C. Ten milliliters of aliquots was taken from each culture at time interval of 0, 1, 3 and 7 d and filtered by the Whatman type C glass fiber paper for measurement of preparation of element. All procedures were done under nonsterilized conditions. Element extraction percentage was obtained by the following equation: (extraction amount of the element (mass/volume)/total amount of the element in the sample (mass/volume)) × 100. The experiments were in duplicate or triplicate, and standard deviations were less than 5% (data not shown). Control test (no refractory sample addition) was also conducted along the bioleaching test; however, blank test was not performed since refractory

addition to deionized water already showed an extreme increase of pH (around 11).

2 Results and discussion

2.1 Element penetration analysis

Figure 4a shows the distribution of elements in the sample at the bed of the opening mouth of the furnace or in sampling spot A. Since the opening mouth was the place where waste aluminium products were thrown in, it always had direct contact to solid state of aluminium. Al showed great penetration to 3 cm depth and indicated possibility of more penetration. Na, Mg, and Si of surface, 1 cm depth, and 3 cm depth also showed higher concentration than that of unused refractory. Mg and Si are used for producing aluminium alloy so that they showed higher concentration than those in unused (virgin). Na might come from aluminium waste such as waste aluminium window frames and waste aluminium wheels for cars. Fig.4b shows the distribution of elements in the sample at the under part of the side wall below the level of melting aluminium or in sampling spot B. This is the place which was always submerged in melting aluminium unless the furnace was out of service due to repair. Na, Mg, Al, Si, and Ca of surface, 1 cm depth, and 3 cm depth were found in higher concentration than those in unused refractory sample. This is also the place where all contaminants would be accumulated; therefore, a broad variety of elements was found in higher concentration than those in unused refractory sample. Ca might come from inside of the refractory. Fig.4c shows the distribution of elements in the sample at the upper part of the side wall near the ceiling or in sampling spot C. Direct contact to Al in solid and melting states did not occur in this place and Al in only gaseous state will reach to this place. Al concentration on surface of the refractory did not show the highest but almost equal to the concentrations at 1 and 3 cm depth, which might imply that surface contamination was not significant and it was the same level as penetration of elements. Al apparently showed deeper penetration than 3 cm depth. Na, Si, and Ca of surface, 1 cm depth, and 3 cm depth were found in higher concentration than that of unused refractory sample. Ca was evaporated and easily became gaseous state in the furnace. Ca showed strong penetration into the sample.

Since not only virgin ingot of aluminium but also waste window frames, waste wheels for cars, and other waste products made by aluminium were melted in the furnace,

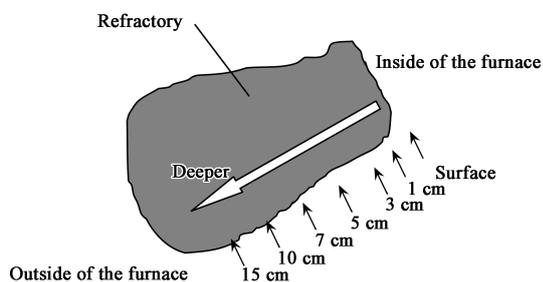


Fig. 3 Depth for scraping the refractory.

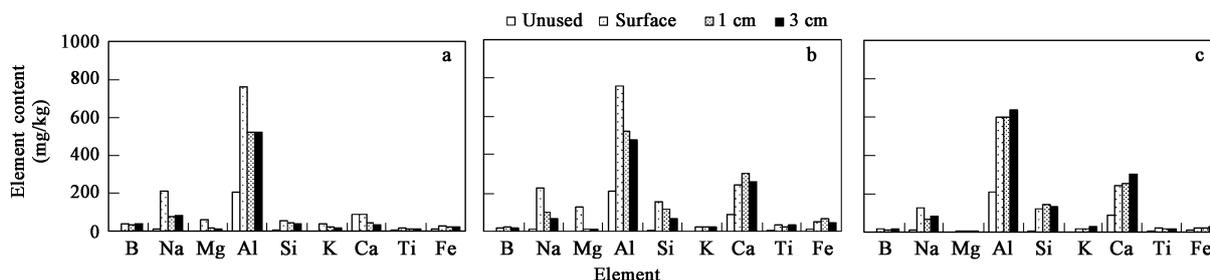


Fig. 4 Element distribution in the sample at sampling spot A (a), sampling spot B (b), and sampling spot C (c).

various contaminants were expected in the furnace. The state of Al was different at each sampling spot. Al was mainly in the states of solid, melting, and gas at the sampling spots A, B, and C, respectively. The difference of the states of Al might influence element distribution in the refractory. Al at the sampling spot A showed the same behavior as that at the sampling spot B. Al concentration on the surface was very high and indicated that surface attachment of Al was very active at the sampling spots A and B. Unlike the sampling spot B, other contaminants such as Na, Mg, Si, and Ca were, however, not high at the sampling spot A. Surface attachment might not be so active at the sampling spot C and, like the sampling spot B, contamination by the other elements was relatively high. Contamination by gaseous elements showed that surface attachment and penetration to the refractory proceeded almost equally at the spot. Penetration of elements should be clarified for estimating contamination of refractory. Fig.5 shows penetration of elements at the sampling spot C. According to the figure, Al concentration at surface showed the highest concentration and the concentrations at 1, 3, and 5 cm depths were still very high comparing to the concentration of virgin sample. The highest concentration at the surface sample simply attributed to analysis of a different sample from the one used in Fig.4c. At 7 cm depth, the concentration finally became the same as the

concentration of unused sample and the concentrations at 10 and 15 cm depths showed as low as the concentration of unused sample. The similar trends were seen for other elements. Consequently, it could be said that penetration of elements would reach to almost 7 cm depth. Practically, the refractory located surface to 7 cm depth should be treated for recycling and the refractory located at deeper than 7 cm can be recycled without treatment.

2.2 Bioleaching test

2.2.1 Bioleaching of aluminium melting furnace refractory

Leaching performance of Al, Si, Ca, Na, Mn, and Zn was observed because relatively high amount extraction of those elements was found. The result of bioleaching by the strain ATCC23270 was shown in Fig.6. Three to 10 g of aluminium melting furnace refractory at the sampling spot C was treated. Sample at the sampling spot C was chosen because penetration of elements showed the highest among the three spots (Fig.4). High leaching rate was shown on Al, Si, and Ca, on the other hand, almost no leaching was seen on Na, Mn, and Zn. Among Al, Si, and Ca, addition of 10 g showed low leaching performance and clearly implied inhibition of bioleaching. The result of bioleaching by the strain TM-32 is shown in Fig.7. One to 3 g of aluminium melting furnace refractory at the sampling spot C was treated. Larger amount, 5 and 10 g, used for the strain ATCC23270 could not be treated by the strain TM-32. Element leaching was occurred on all the elements. Leaching percentage was very high especially on Al and Si, and the high leaching performance was shown on 1, 2, and 3 g addition. Comparing the leaching performance between the strains ATCC23270 and TM-32, larger amount of refractory was treated by the strain ATCC23270 than by the strain TM-32; however, extraction percentage by the strain TM-32 was higher than by the strain ATCC23270 when Figs.6 and 7 are compared. The trend of the extraction could be explained by pH difference between the two cultures. The pH of the strain TM-32

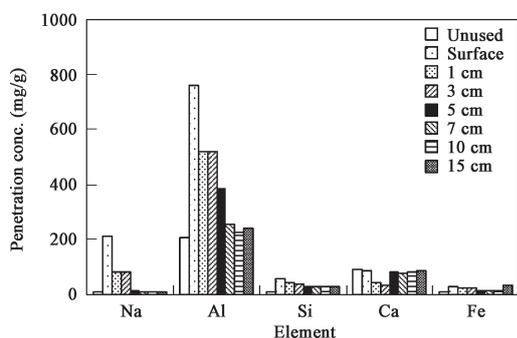


Fig. 5 Penetration of elements at sampling spot C.

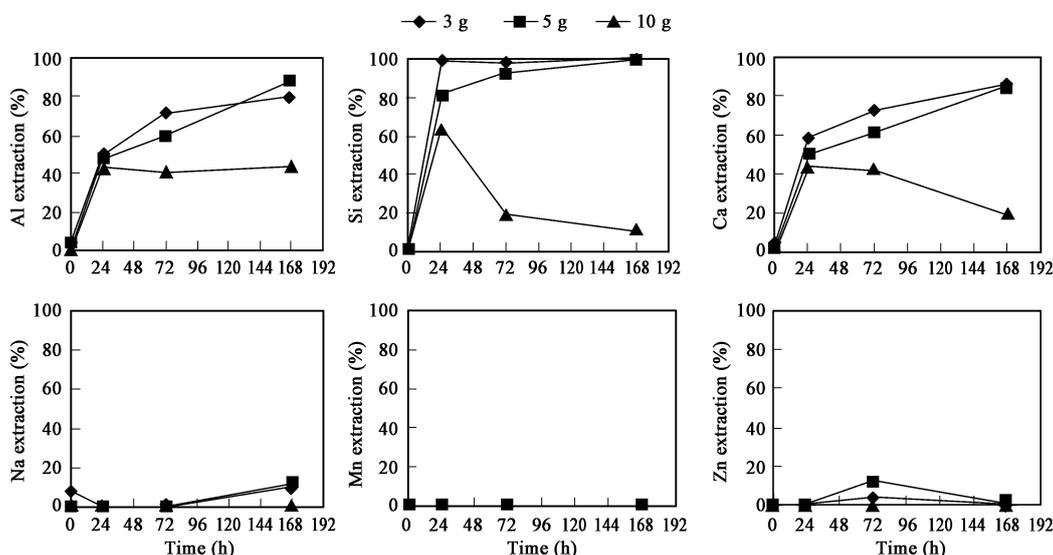


Fig. 6 Element extractions from aluminium melting furnace refractory by the strain ATCC23270.

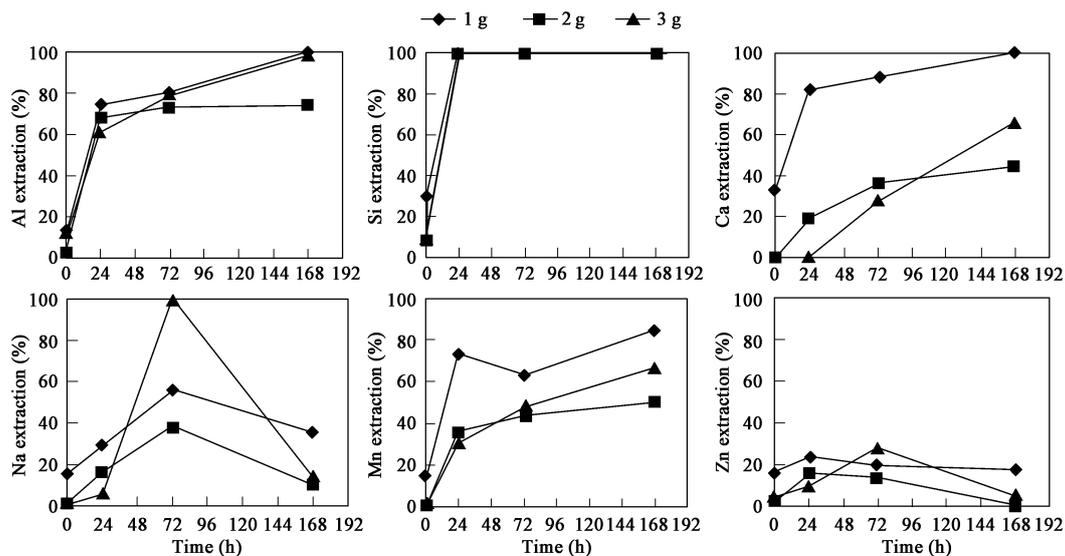


Fig. 7 Element extractions from aluminium melting furnace refractory by the strain TM-32.

showed as low as 1 after 288 h; whereas, the one of the strain ATCC23270 showed the range from nearly 2 to over 3. Since bioleaching mechanism depends on Eh-pH diagram of elements, the lower pH usually provides advantage to element extraction (Chida, 1996). The element of Mn, for example, was not leached by the strain ATCC23270 at all but high leaching percentage was shown by the strain TM-32. It might be explained as follows (Chida, 1996). Mn^{4+} cannot be extracted by SO_4^{2-} but can be done by SO_3^{2-} . SO_3^{2-} is produced on the way that *A. thiooxidans* produces SO_4^{2-} from S^0 . That is why Mn leaching could be observed in the treatment by the strain TM-32.

2.2.2 Bioleaching of copper melting furnace refractory

Leaching performance of Cu, Zn, Al, and Si was observed here. The result of bioleaching by the strain ATCC23270 is shown in Fig.8. Three to 10 g of copper melting furnace refractory was treated. For all the ele-

ments, the highest leaching performance was shown on 3 g of addition and the lowest performance was shown on the 10 g addition. In the case of Zn, high leaching performance was seen on 3, 5, and 10 g addition. The result of bioleaching by the strain TM-32 is shown in Fig.9. One to 3 g of copper melting furnace refractory was treated. One gram addition of the refractory showed the highest leaching performance and 3 g addition gave the lowest performance. Comparing the leaching performance between the strains ATCC23270 and TM-32, larger amount of refractory was treated by the strain ATCC23270 than by the strain TM-32, and extraction performance by the strain ATCC23270 was higher than by the strain TM-32 according to Figs.8 and 9. The strain TM-32 culture could not provide proper environment for element extraction. For example, 3 g of addition resulted pH 3.5 and about 500 mV in the strain ATCC23270 culture and over 4.0 and about 400 mV in the strain TM-32 culture at 240 h for

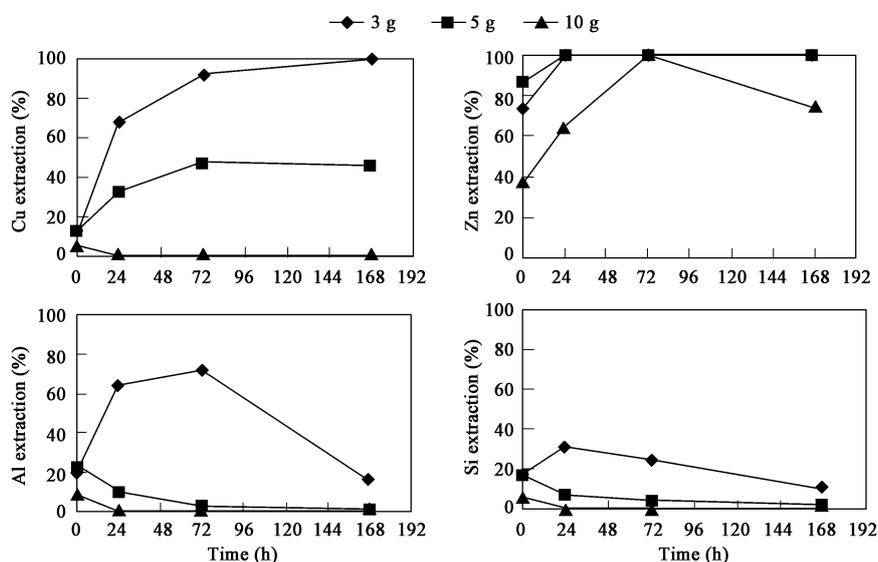


Fig. 8 Element extractions from copper melting furnace refractory by the strain ATCC23270.

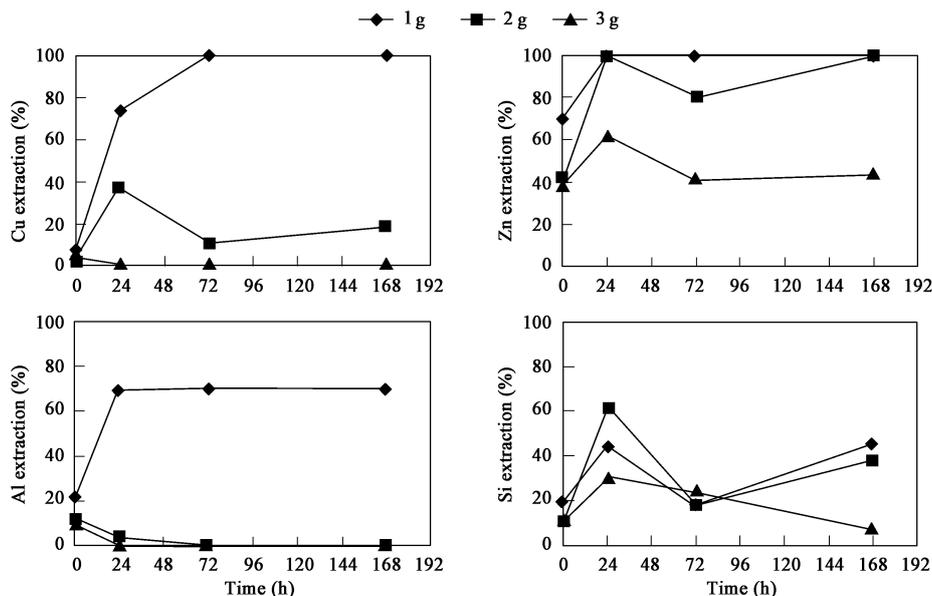


Fig. 9 Element extractions from copper melting furnace refractory by the strain TM-32.

pH and ORP, respectively. Zn extraction was high in the both cultures, which may attribute to its low boiling point. Because of its low boiling point, Zn tended to accumulate on near the surface of the furnace where wash-out is easily occurred (Fukunaga *et al.*, 1996). Zn extraction in Figs.8 and 9 occurred already at the time 0; this phenomenon might support the argument stated above. Bioleaching of spent refractory of copper melting furnace by the mixed culture of the strains ATCC23270 and TM-32 was done (data not shown). The result of element extraction by the mixed culture showed almost the same trend as that by the strain ATCC23270. This result was different from the

one in Ishigaki *et al.* (2005) and the mixed culture showed the best extraction performance rather than pure cultures in their study. The difference came from culture environment. The final pH and ORP in the cultures were less than 3.5 and more than 510 mV and more than 3.0 and less than 300 mV for Ishigaki *et al.* (2005) and this study, respectively. The mixed culture in this study could not maintain lower pH and higher ORP than pure cultures did.

Leaching performance on Al and Si between in aluminium and copper melting furnace refractories was compared. Comparing Figs.6, 7 and 8 and Figs.7, 8 and 9, the performance in aluminium melting furnace refractory was

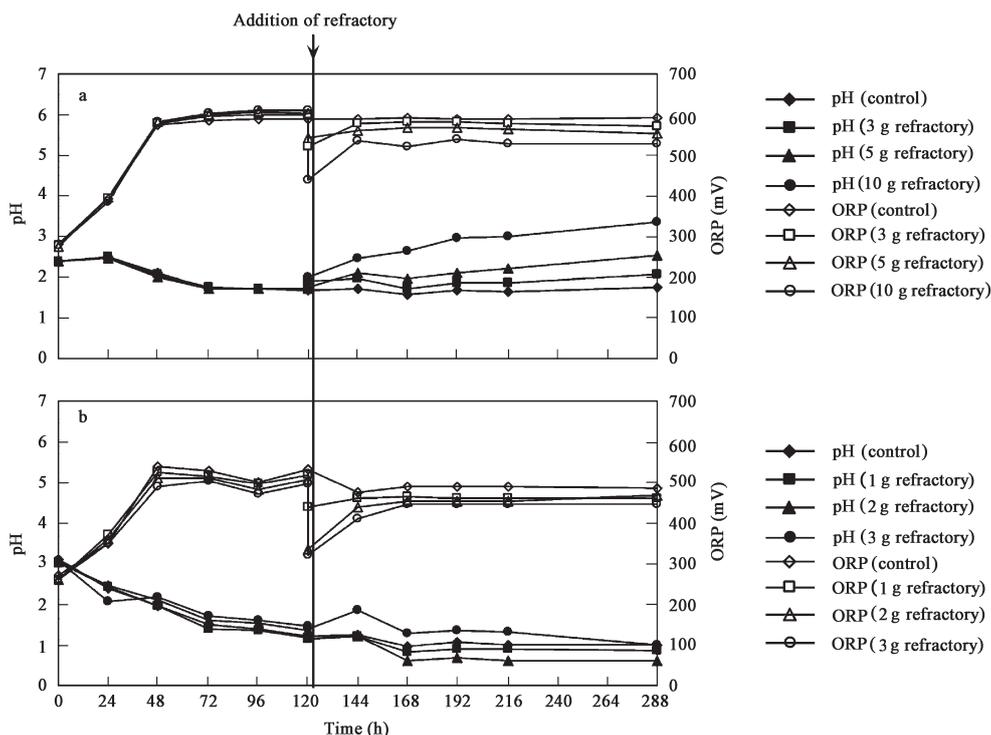


Fig. 10 pH and ORP changes with addition of spent refractory of aluminium melting furnace by strain ATCC23270 (a) and strain TM-32 (b).

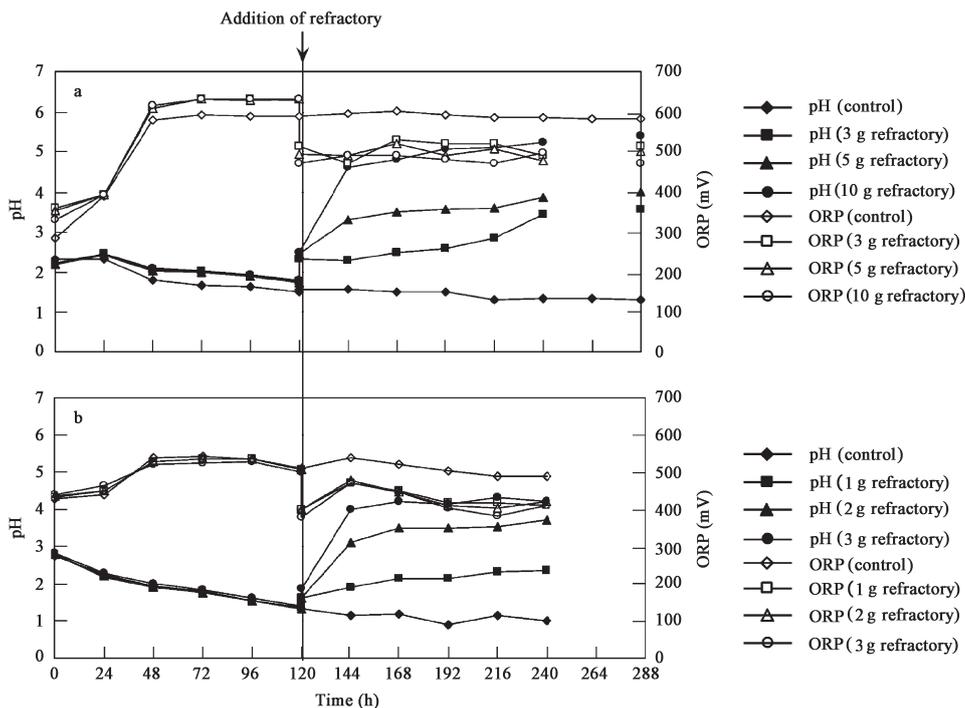


Fig. 11 pH and ORP changes with addition of spent refractory of copper melting furnace by strain ATCC23270 (a) and strain TM-32 (b).

better than that in copper melting furnace refractory. The characteristics of the refractories might cause the difference in the performance. According to Figs.10 and 11, pH increase was drastic in copper melting furnace refractory which had more alkali content than the aluminium melting furnace refractory did, and then, the copper melting furnace refractory inhibited the activity of the both strains which resulted in a poor performance of element leaching from copper melting furnace refractory. Comparing the leaching performance between the strains ATCC23270 and TM-32, larger amount of refractory was treated by the strain ATCC23270 than by the strain TM-32.

3 Conclusions

The following conclusions are drawn from the results of this study.

Element penetration into melting refractory was seen and was 7 cm from the surface. Contaminated part of refractory should be treated before recycling and the refractory located deeper from the penetration limit can be sent for recycling without treatment.

Leaching performance of elements was different in kinds of melting refractory and of a bacterium used. Bioleaching of aluminium melting furnace refractory showed the better performance than that of copper melting furnace refractory did. *A. ferrooxidans* ATCC23270 could treat

larger amount of the refractories than *A. thiooxidans* TM-32 could do.

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