Analysis of Heavy Metals in a Tailing Impoundment of Abandoned Mn Mine by Using Two Sequential Extractions∗

Kyoungkeun Yoo1,∗, Keiko Sasaki2, Tsuyoshi Hirajima1 and Masami Tsunekawa1

1Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan
2Laboratory of Environmental Science, Otaru University of Commerce, Otaru 047-8501, Japan

The tailing impoundment was investigated for vertical distribution of minerals by X-ray fluorescence analysis (XRF), powder X-ray diffraction (XRD), and two sequential extraction methods. It was found that Si, Mn, and Fe occupied over 80% in mass balance of XRF, and present as constituents of clay minerals, oxides, and pyrite, respectively. Therefore, the sampling site was regarded as chemically stable. Two sequential extraction methods were complementary to each other, therefore, the combination of two methods is useful for further analysis of sediments including variable minerals.

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1. Introduction

Tailing impoundments have been regarded as an origin of mine pollution. Therefore, sediments in tailing impoundments have been examined because chemical forms of heavy metals influence the environmental stability of tailing impoundments. The sequential extraction methods have been adopted for tailing analysis for the reason that the methods are very useful for characterizing crystalline and uncrystalline elements in soil and sediments.

Huerta-Diaz and Morse1) had developed the acid sequential extraction and categorized the sediments as reactive, silicate, and sulfide fractions, where a portion of the extracted reactive fraction would actually influence the stability of the abandoned mines. However, in this method, the reactive fraction was not characterized in detail of its chemical forms. Tessier et al.2) had developed the selective sequential extraction for the bottom sediment of river, and this method was useful for analysis of chemical species with relatively weak binding such as carbonate and oxide type with one of Fe and Mn mineral. It is important to characterize the chemical details of the reactive zone in mine tailing impoundments for the purpose of evaluation of the fate of environmental impact at that place. Therefore, in the present study, a tailing impoundment in Hokkaido, Japan was investigated by the combination of two sequential extractions and, each result was compared and discussed.

2. Experimental

2.1 Site descriptions and sampling

The sampling site, which is the tailing impoundment of abandoned Mn mine, is located in the west of Otaru city, Japan. Since the wastewater of high Mn concentration has been discharged from adit of abandoned Mn mine, the wastewater has been treated with alkali reagents to bring the pH to 10. Mn has been, therefore, dumped into the tailing impoundment as end products of the treatment processes as well as gangues of mining. No plant is grown in the tailing impoundment. Hence, there would be lacking in the nutrients for the heterotrophic microorganisms which contribute to the fixation of heavy metals.

Sediment cores were taken vertically at every 40 cm in depth along a 400 cm profile in July 2000. To avoid the oxidation of samples, nitrogen gas was injected to each sampling pack. All sediments were dried overnight at 60°C ground with a tungsten carbide ball mill, and then separated with 100 mesh-sieving to supply the under size fractions for powder X-ray diffraction, X-ray fluorescence analysis and the sequential extractions.

2.2 XRD and XRF analyses

The mineralogy of all samples was investigated with Horiba MESA-500 X-ray fluorescence spectrometer (Japan) and JEOL JDX-3500 X-ray diffractometer (Japan), respectively. X-ray diffraction data were collected with a monochromator under the following conditions: radiation, Cu Kα, 30 kV, 200 mA; step scanning method; time constant, 0.5 s; angle range, 2.5–65 deg/2θ, and X-ray fluorescence was conducted under the following conditions: Cu Kα, 50 kV and 50 mA; energy diffusive type.

2.3 Sequential extraction

Two sequential extractions were adopted to determine the chemical forms of trace elements. In these methods, the solid samples can be classified into specific fractions which can be selectively extracted by using appropriate reagents as follows.

One method was developed by Huerta-Diaz and Morse1) and was modified by Sasaki et al.3) 2.5 g of each dried sample was first extracted with 1 mol dm−3 HCl (10 cm3) for 16 h, then with 46%HF (30 cm3) and boric acid (5 g) for 16 h, and finally with 70% nitric acid (10 cm3) for 2 h. All processes were carried out at room temperature.

The other method was developed by Tessier et al.2) and was modified by Xi Li et al.4) 1 g of each dried sample was ex-
trated with the following reagents and conditions: 1) 8 cm$^3$ of 1 mol dm$^{-3}$ MgCl$_2$ (adjusted to pH 7) for 1 h at room temperature in a shaker, 2) 8 cm$^3$ of 1 mol dm$^{-3}$ NaOAc (adjusted to pH 5) for 5 h at room temperature in a shaker, 3) 20 cm$^3$ of 0.4 mol dm$^{-3}$ NH$_3$-OH·HCl (in 25% HOAc) for 6 h at 96°C in a water bath, 4) first 3 cm$^3$ of 0.02 mol dm$^{-3}$ HNO$_3$ and 5 cm$^3$ of 30% H$_2$O$_2$ (adjusted to pH 2) for 2 h at 85°C in a water bath, then 3 cm$^3$ of 30% H$_2$O$_2$ (adjusted to pH 2) for 3 h at 85°C in a water bath, and finally 5 cm$^3$ of 3.2 mol dm$^{-3}$ NH$_4$OAc (in 20% HNO$_3$) and about 4 cm$^3$ deionized water for 30 min at room temperature in a shaker, 5) 7 cm$^3$ of concentrate nitric acid, 2.5 cm$^3$ of 46% HF, and 0.5 cm$^3$ of 30% H$_2$O$_2$ for 20 min at 210°C in a microwave (Milestone Co. Ltd., Japan).

All extracted solutions were separated by centrifugation for 30 min at 10000 rpm, and then the supernatants were taken to analyze with a SEIKO SPS 7800 inductively coupled plasma atomic emission spectroscopy (ICP-AES). All elements in each extracted fraction were expressed as milligram per one gram of dry sediment.

2.4 Contents of organic matter

The contents of organic matters in sediments were estimated by the weight difference before and after heating the dry samples for 2 h at 600°C.5)

2.5 Evaluation of sulfate reducing bacteria activity

The distribution of sulfate-reducing bacteria (SRB) was determined with a biochecker-S (San-Ai Oil Co., Japan). This kit consists of a capillary tube and a reagent body, which reacts with SRB propagated in a sample, and then shows black precipitation on the wall of itself when SRB are active. One kit was cultivated in an incubator at 30°C for three days, and then the extent of precipitate formation was evaluated by observing. This precipitate would result from the reason that ferrous component in the reagent body react with hydrogen sulfide by metabolism of SRB.

3. Results and Discussion

As shown in Table 1, all samples were analyzed qualitatively by XRF. This shows that Si, Mn and Fe occupy over 80% in all depths and that high Mn content is characteristic to the tailing impoundments. The results were referred to select the elements which should be analyzed by ICP-AES measurements in the process of sequential extraction.

Figure 1(a) shows the XRD pattern of the sample in 40–80 cm depth, since all sample have similar XRD patterns independent of depth. XRD measurements were conducted to examine mineralogy of Si, Mn, Fe and other trace elements. There is, however, no peaks observed except for quartz. Accordingly, Mn and Fe would be non-crystalline forms that could not be detected by XRD, and it was impossible to elucidate the chemical forms only by XRD. Therefore, the selective sequential extraction was performed for characterization of the associated forms of Fe, Mn, and other trace metals, and the results were discussed as below.

Figures 2(a), (c), and (d) show that fractions of Mn, Pb, and Ca were extracted considerably with HCl–namely, the reactive fraction. As shown in Figs. 2(a), (b), and (c), the reactive fractions of Mn, Pb and Fe have the similar trends, and particularly, Pb shows clearly that the extracted portion distributes markedly in upper zone (0–100 cm), which would suggest that the sediments near surface were easily weathered and then changed into reactive materials. Although it is observed that Mn and Fe distribution are not uniformly except the surface in Figs. 2(a) and (b), it was impossible to characterize exactly their chemical forms and potential effects by Huerta-Diaz’s method.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Si</th>
<th>Mn</th>
<th>Fe</th>
<th>Al</th>
<th>K</th>
<th>S</th>
<th>Ca</th>
<th>Zn</th>
<th>Others</th>
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<tr>
<td>0–40</td>
<td>38.0</td>
<td>21.4</td>
<td>24.7</td>
<td>3.41</td>
<td>2.99</td>
<td>1.99</td>
<td>1.13</td>
<td>2.04</td>
<td>4.34</td>
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<tr>
<td>40–80</td>
<td>35.4</td>
<td>27.0</td>
<td>22.3</td>
<td>3.15</td>
<td>2.55</td>
<td>2.34</td>
<td>1.57</td>
<td>1.87</td>
<td>3.82</td>
</tr>
<tr>
<td>80–120</td>
<td>39.9</td>
<td>26.3</td>
<td>17.6</td>
<td>3.27</td>
<td>2.70</td>
<td>2.61</td>
<td>2.74</td>
<td>2.69</td>
<td>2.19</td>
</tr>
<tr>
<td>120–160</td>
<td>41.0</td>
<td>23.4</td>
<td>18.3</td>
<td>3.82</td>
<td>3.49</td>
<td>2.18</td>
<td>2.69</td>
<td>1.35</td>
<td>3.77</td>
</tr>
<tr>
<td>160–200</td>
<td>39.1</td>
<td>25.6</td>
<td>17.7</td>
<td>4.21</td>
<td>3.56</td>
<td>2.09</td>
<td>3.63</td>
<td>0.96</td>
<td>3.15</td>
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<tr>
<td>200–240</td>
<td>37.9</td>
<td>25.8</td>
<td>18.7</td>
<td>4.20</td>
<td>3.49</td>
<td>2.13</td>
<td>3.37</td>
<td>1.25</td>
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<tr>
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<td>36.1</td>
<td>26.9</td>
<td>19.0</td>
<td>4.14</td>
<td>3.39</td>
<td>2.18</td>
<td>3.66</td>
<td>1.31</td>
<td>3.32</td>
</tr>
<tr>
<td>280–320</td>
<td>34.6</td>
<td>28.4</td>
<td>19.7</td>
<td>3.76</td>
<td>3.05</td>
<td>2.05</td>
<td>3.59</td>
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<tr>
<td>320–360</td>
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<td>25.2</td>
<td>18.0</td>
<td>4.10</td>
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<td>360–400</td>
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<td>18.2</td>
<td>4.25</td>
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<td>2.22</td>
<td>3.58</td>
<td>1.13</td>
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</table>
Figures 2(e), (f), and (g) show that most Si, Al, and K were extracted by HF (namely the silicate fraction). The HF-fraction of Si mostly corresponds to quartz as clearly detected by XRD, and distributed uniformly independent of depth. The HF-fractions of Al and K would be assigned to clay minerals, though they were not detected by XRD, and a part of the HF-fraction of Si would also be involved in them. The clay minerals were much more distributed under $-100 \text{ cm}$ in depth.

Fe was considerably detected in all extraction fractions, and the distribution of Fe has a similar trend with those of S and Zn in the HNO$_3$-extracted fraction (See Figs. 2(b), (h), and (i)). Figure 3 shows that the molar ratio of Fe to S extracted with HNO$_3$ is very close to 1:2. XRD pattern after HF-extraction is indicated in Fig. 1(b), where pyrite (FeS$_2$) peaks were very sharply detected after quartz was extracted away with HF. Accordingly, these results suggest that Fe, S, and Zn are compositions of pyrite and other metal sulfides. Fortin and Beveridge$^6$ have reported that SRB reduce sulfate into sulfide in anaerobic zone of tailing ponds, and that the subsequent precipitation of Fe and other metal sulfides can greatly lead the fixation of heavy metals released by biotic and abiotic oxidation of sulfides in aerobic zone. The overall process of microbial reduction of sulfate can be represented by the following equation:

$$2(\text{CH}_2\text{O}) + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-,$$

where $\text{CH}_2\text{O}$ represents organic matter, and $\text{H}_2\text{S}$ and $\text{HCO}_3^-$ are the metabolic end products. Since organic matter is a prerequisite for metabolism by SRB as described in eq. (1), the distribution of organic matter should be related to those of SRB activity. Figure 4 shows the vertical distribution of organic matter and the contents of HNO$_3$-extracted S which was
obtained by sequential extraction. The results indicate that both trends are in accord. In the SRB check test, SRB activity was strongly detected in the upper zone (0–100 cm), but not in other zone. Therefore, it is suggested that the microbial activity of SRB might affect to the formation of the HNO$_3$-extracted S in the tailing impoundment.

By using Huerta-Diaz’s method, Si, Al, K, and parts of S, Fe, Zn were determined to be the constituents of clay minerals and metal sulfides. However, the more details of chemical forms of Mn and Fe were not elucidated in the reactive fraction where about 90% of Mn was present in that fraction. It is generally known that Tessier’s method is suitable for comparison of relatively weak bindings of elements in sediments.

Figure 5 shows the result of the vertical distributions of Mn, Fe, Ca, S, Zn, and Si by Tessier’s method. As shown in Figs. 5(a) and (b), Mn and Fe are the most extracted in the oxide-bound fraction, and their relationship is expressed in Fig. 6, indicating a strong positive correlation. This would result

![Fig. 3](image-url)  
Interrelation of HNO$_3$-extracted Fe and S in Herta-Diaz’s acid sequential extraction.

![Fig. 4](image-url)  
Vertical distribution of organic matter and HNO$_3$-extracted sulfur in Heurta-Diaz’s acid sequential extraction.

![Fig. 5](image-url)  
Vertical distribution of (a) Mn, (b) Fe, (c) Ca, (d) S, (e) Zn, and (f) Si by Tessier’s sequential extraction.
from the reason that Mn$^{2+}$ and Fe$^{3+}$ ions in mine drainages would be changed into oxides with an increase in pH by adding alkali reagents for wastewater treatment. There may be also the concomitant precipitation of Mn-hydroxides with Fe-compounds.

From Fig. 5(c), Ca was extracted mostly in the exchangeable fraction, and the extracted portion is relatively smaller in the upper −100 cm zone. This might suggest that Ca was dissolved and then swept away by weathering at the surface.

As shown in Figs. 5(d) and (e), S and Zn were mostly extracted in the residual fraction, and they show similar distributions with the HNO$_3$ fraction of Huerta-Diaz’s method (Figs. 2(h) and (i)). Therefore, S and Zn extracted in the residual fraction would be correspondent to sulfide minerals. Figure 5(f) shows that Si is also extracted mostly in the residual fraction, and the contents ranges between 200 and 300 mg·g$^{-1}$. This is in good agreement with the results of Fig. 2(e).

As discussed above, the results of sequential extractions by Tessier’s method gave further detail information on portions extracted in the reactive fraction by Huerta-Diaz’s method. Considering that the main components (Si, Mn, and Fe) dis-

![Graph](https://example.com/graph.png)  
*Fig. 6* Interrelation of Mn and Fe contents of the bound to oxides-fraction in Tessier’s sequential extraction.

![Graph](https://example.com/graph.png)  
*Fig. 7* Comparison between HCl-extraction in Huerta-Diaz’s method(solid circle) and 1st–4th fractions in Tessier’s method(bars) for (a) Mn, (b) Fe, (c) Zn, (d) S.
tribute as soil minerals, hydroxides, and sulfides in tailing impoundment, the sampling site would be chemically stable.

Figure 7 shows the comparison between both sequential extraction methods for Mn, Fe, Zn and S. The results indicate that the amount of first fraction, that is, HCl-extractable, is fairly correspondent to sum of ion-exchangeable, bound to carbonate, oxides, and organic matters in Tessier’s method. The former is suitable to partition the relatively strong binding of heavy metals in the sediment. On the contrary, the latter is used to elucidate the partition of relatively weak binding of heavy metals. These methods should be used complementarily each other.

4. Conclusion

The vertical distributions of minerals in the tailing impoundment in Hokkaido, Japan was examined by XRF, XRD, and the sequential extractions. Only use of XRD and XRF is nothing but analysis of elemental compositions and minerals distributed in the tailing impoundment. By addition of two sequential extractions, all chemical forms of trace elements were also elucidated. Huertz-Diza’s method and Tessier’s method compensated each other, and the combined method was useful for analysis of tailing impoundments. It was concluded that Si, Mn, and Fe were the main components and present as silicates, oxides, and sulfides, respectively, therefore, the tailing impoundment was regarded as stable.

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REFERENCES