Solubility of metals content bangka tin tailings sand using inorganic acids

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Abstract. Research entitled Solubility of Metals Content Bangka Tin Tailings Sand Using Inorganic Acids The sample used was tailings sand from tin mining on Bangka Island which was destroyed using several variations of inorganic acids alone, H2SO4, HNO3 and HCl and mixed with H2SO4-HCl, H2SO4-HNO3, HNO3-HCl and H2SO4-HNO3-HCl. Metal content characterization was analyzed using XRF. From the results of the analysis, it was found that the average heavy metals and rare earth metals were more in HNO3 while for a mixture of acids, namely the use of H2SO4-HNO3.

1. Introduction

The Province of the Bangka Belitung Islands is very well known for its tin-producing areas. With an area of 1.6 million hectares of the Bangka Belitung Islands, 3/4 of its area is included in large-scale and unconventional Mining Business Permits. Tin mining in the Province of the Bangka Belitung Islands produces the most tin in Indonesia and is the world's second largest after China. Tin mining produces a fine-grained mixture of particles taken from the ore and water used in the refining process known as tailings, which range from 0.001-0.6 mm.

This tin mining tailings has a potential rare earth metal content (REE) which is estimated to reach seven million tons. Minerals that have economic value are ilmenite (32.43%), zircon (16.65%), cassiterite (12.59%) and monazite (11.76%). Monacite (Ce, La, Y, Th)PO3) is a phosphate compound of REE which contains 50-70% oxide of REE. These minerals become by-products (slag) of tin ore processing [1,2].

To separate the metal content in the tailings sand, an extraction process is needed by dissolving it with inorganic acids [3-9] for further use. In this study, three types of inorganic acids were used, namely hydrochloric acid (HCl), sulfuric acid (H2SO4) and nitric acid (HNO3) which were used alone or together. To identify the solubility of these metals against the use of inorganic acids were characterized using XRF (X-Ray Fluorecence).

2. Method

Samples of tailings resulting from tin mining activities were taken from the Banga Island area and then dried. Then extracted using several variations of acid, namely HCl [3,10], H2SO4 [9] and HNO3 [10] with the same concentration of 3 N. Then analyzed using XRF before and after extraction.
3. Result and Discussion

The tailings sand sample was destroyed using several variations of acids as presented in Table 1. The acid was varied to see the solubility of the metals contained in it against the acid used. After being extracted, it was dried using a hotplate and heated. The resulting precipitate was analyzed using XRF.

Table 1. Solubility of metals in the use of various types of inorganic acids

| Type of acids            | Ba  | Ca* | Cd  | Cu  | Fe** | Mn* | Pb  |
|-------------------------|-----|-----|-----|-----|------|-----|-----|
| Initial sample          | 129.01 | 151.22 | 105.42 | 20.70 | 258.03 | 102.49 | 183.17 |
| H2SO4                   | 38.65 | 52.63 | 78.53 | 8.20 | 186.01 | 22.09 | 170.60 |
| HNO3                    | 17.9 | 66.98 | 83.33 | 4.04 | 121.81 | 19.48 | 38.00 |
| HCl                     | 33.24 | 62.94 | 86.01 | 6.13 | 193.17 | 33.59 | 57.07 |
| H2SO4-HCl               | 34.32 | 68.78 | 74.44 | 4.35 | 147.75 | 21.08 | 45.22 |
| HNO3-HCl                | 30.47 | 64.58 | 86.15 | 5.649 | 121.72 | 19.87 | 36.99 |
| H2SO4+HNO3              | 33.42 | 82.38 | 82.71 | 2.73 | 175.45 | 19.29 | 37.93 |
| H2SO4-HCl-HNO3          | 32.23 | 68.52 | 96.70 | 6.514 | 130.32 | 27.62 | 42.43 |

Note: * in tens, ** in hundreds

From the graph of the solubility of metals against several variations of the type of acid used, it can be seen that there are differences in the strength of the acid in dissolving heavy metals contained in the tailings sand resulting from tin mining. For Ba metal, the most dissolved into HNO3 as much as 109.11 ppm or 86.12% and HNO3-HCl at 76.38% for a mixture of acids.

![Figure 1. Graph of the solubility of metals against various types of acids](image)

The highest solubility of Ca metal was in the use of H2SO4 of 985.9 ppm or 65.20%, while for the mixture the highest was in the use of HNO3-HCl of 866.4 ppm or 57.29%. The highest solubility of Cd metal was in the use of H2SO4 at 26.89 ppm or 25.50%, while for a mixture of acids the most was H2SO4-HCl at 30.98 ppm or 29.39%. The highest solubility of Cu metal was in the use of HNO3 at 16.66 ppm or 80.51%, while for a mixture of acids the highest was in H2SO4-HNO3 at 17.97 ppm or 86.81%.

For Fe metal, the highest solubility of Fe is using HNO3 of 13,622 ppm or 52.79% while for mixtures using HNO3-HCl with a solubility of 13,631 ppm or 52.83%. The highest solubility of Mn metal was in the use of HNO3 of 830.1 ppm or 80.99%, while for the mixture the highest solubility was in the use of H2SO4-HNO3 of 832 ppm or 81.18%. The solubility of Pb metal has the highest solubility in the use of
HNO₃ of 145.17 ppm or 79.26%, while for a mixture of acids the highest solubility is in the use of HNO₃-HCl of 146.18 ppm or 79.81%.

Table 2. Percentage of solubility of metals in the use of various types of acids

| No | Type of Acid     | Ba (%) | Ca (%) | Cd (%) | Cu (%) | Fe (%) | Mn (%) | Pb (%) |
|----|------------------|--------|--------|--------|--------|--------|--------|--------|
| 1  | H₂SO₄           | 70.04  | 65.20  | 25.50  | 60.37  | 27.91  | 78.45  | 6.86   |
| 2  | HNO₃            | 86.12  | 55.71  | 20.95  | 80.51  | 52.79  | 80.99  | 79.26  |
| 4  | HCl              | 74.24  | 58.38  | 18.41  | 70.40  | 25.14  | 67.23  | 68.84  |
| 5  | H₂SO₄-HCl       | 73.40  | 54.52  | 29.39  | 78.98  | 42.74  | 79.43  | 75.31  |
| 6  | HNO₃-HCl        | 76.38  | 57.29  | 18.27  | 72.72  | 52.83  | 80.61  | 79.81  |
| 7  | H₂SO₄-HNO₃      | 74.10  | 45.52  | 21.54  | 86.81  | 32.00  | 81.18  | 79.29  |
| 8  | H₂SO₄-HCl-HNO₃  | 75.02  | 54.69  | 8.27   | 68.54  | 49.49  | 73.05  | 76.84  |

![Figure 2. Graph of the percentage solubility of metals against various types of acids](image-url)

From these data, it can be seen that of the seven metals the solubility is greatest in HNO₃, which is Ba, Fe, Mn, Cu and Pb, while the second highest is in the use of H₂SO₄ namely Ca and Cd metals and the weakest is HCl. Nitric acid is a strong acid from inorganic materials which is included in monoprotic acid where the pKa of nitric acid is 1.4 smaller than sulfuric acid 1.98 and hydrochloric acid 6.3. This is one of the more metals solubility factors in nitric acid. Sulfuric acid and hydrochloric acid in group I metals such as Pb, Hg and Ag can form precipitates, and also for barium metal will precipitate in the presence of sulfuric acid.

The solubility of rare earth metals to various acid variations is presented in table 2. The solubility of Hf metal has the greatest solubility in the use of HCl of 12.89 ppm and 15.8 ppm for a mixture of H₂SO₄-HNO₃ acids.
Table 3. Solubility of some REE with various acid variations

| Type of acid           | Hf (ppm) | Ti** (ppm) | Ce* (ppm) | Th (ppm) | Yb (ppm) | U (ppm) |
|------------------------|----------|------------|-----------|----------|----------|---------|
| Initial Sample         | 25.48    | 72.62      | 62.56     | 109.65   | 8.05     | 13.61   |
| H_2SO_4                | 17.84    | 59.44      | 43.53     | 113.42   | 0        | 9.06    |
| HNO_3                  | 12.88    | 59.35      | 41.12     | 78.62    | 5.42     | 5.11    |
| HCl                    | 12.59    | 60.48      | 41.18     | 81.27    | 4.69     | 8.49    |
| H_2SO_4-HCl            | 11.77    | 59.78      | 45.73     | 82.86    | 5.86     | 6.64    |
| HNO_3-HCl              | 10.58    | 60.07      | 36.55     | 70.48    | 3.49     | 7.12    |
| H_2SO_4-HNO_3          | 9.68     | 57.31      | 42.35     | 81.65    | 0.05     | 7.09    |
| H_2SO_4-HCl-HNO_3      | 12.72    | 61.53      | 44.35     | 82.63    | 6.06     | 6.67    |

Note: * in tens, ** in hundreds

Figure 3. Graph of the solubility of REE against various types of acids

The solubility of Ti was greatest in HNO_3 of 13.27 ppm and of 15.31 ppm in the use of a mixture of H_2SO_4-HNO_3 acids. The solubility of Ce was greatest in HNO_3 at 21.44 ppm and 26.01 in a mixture of HNO_3-HCl acids. The solubility of Th was greatest in the use of HNO_3 at 31.03 ppm and 39.17 in the use of a mixture of HNO_3-HCl acids. The highest solubility of Yb was in the use of H_2SO_4 at 8.05 ppm and 8 ppm in a mixture of H_2SO_4-HNO_3 acids. The greatest solubility of U in the use of HNO_3 is 8.5 ppm and 6.94 ppm in a mixture of H_2SO_4-HCl-HNO_3 acids.

The percentage of Ti solubility was greatest in the use of HNO_3 of 18.27% and 21.08% for a mixture of H_2SO_4-HNO_3 acids. The highest percentage of Ce solubility in HNO_3 was 34.27% and 41.58% in a mixture of HNO_3-HCl acids. The highest percentage of Th solubility was 30.68% using HNO_3 and 37.86% using a mixture of HNO_3-HCl acids. The percentage of Yb solubility was highest in H_2SO_4 at 100% and 99.40% in the use of a mixture of H_2SO_4-HNO_3 acids. The highest percentage of U solubility was 62.48% using HNO_3 and 51.18 using a mixture of H_2SO_4-HCl acids.

Nitric acid is an oxidizing acid capable of dissolving most metals and converting them to soluble metal nitrates. It has a low oxidizing strength below 2 M, but when concentrated, it is a potent oxidizing acid. Using a mixture of acids or a dilute nitric solution, such metals can be dissolved [7,8]. The most
The common use of nitric acid in rock analysis is to breakdown both carbonate and sulfide minerals (usually in association with HCl) [8]. Nitric acid is a colorless, flammable liquid with a throat-drying odor. In the presence of sunshine, both pure nitric acid and its aqueous solutions degrade to produce NO$_2$. Because of the presence of dissolved NO$_2$, old nitric acid samples are frequently yellow or brown.

Table 4. Percentage of solubility of REE in the use of various types of acids

| Type of acid      | Hf (%) | Ti (%) | Ce (%) | Th (%) | Yb (%) | U (%) |
|-------------------|--------|--------|--------|--------|--------|-------|
| Sampel Awal       | 100    | 100    | 100    | 100    | 100    | 100   |
| H$_2$SO$_4$       | 29.97  | 18.15  | 30.42  | 3.32   | 100    | 33.41 |
| HNO$_3$           | 49.45  | 18.27  | 34.27  | 30.68  | 32.71  | 62.48 |
| HCl               | 50.61  | 16.72  | 34.18  | 28.34  | 41.78  | 37.65 |
| H$_2$SO$_4$-HCl   | 53.79  | 17.68  | 26.90  | 26.94  | 27.17  | 51.18 |
| HNO$_3$-HCl       | 58.47  | 17.28  | 41.58  | 37.86  | 56.67  | 47.68 |
| H$_2$SO$_4$-HNO$_3$| 62.00  | 21.08  | 32.30  | 28.01  | 99.40  | 47.88 |
| H$_2$SO$_4$-HCl- HNO$_3$| 50.06  | 15.27  | 29.11  | 27.15  | 24.66  | 51.01 |

From table 4 it can be seen that the percentage of solubility of Hf is greatest in the use of HCl of 50.61% and 62% in the use of a mixture of H$_2$SO$_4$-HNO$_3$ acids.

Figure 4. Graph of the percentage solubility of REE against various types of acids

The most commonly used halogen acid for dissolving geologic materials is hydrochloric acid (HCl). HCl, unlike HNO$_3$, is a weak reducing acid that isn't commonly utilized to break down organic compounds. Carbonates, phosphates, various metal oxides, and metals all respond well to it [13]. Hydrochloric acid's capacity to dissolve metal oxides like iron and manganese oxides is linked to the chloride ion's ability to complex, and most chloride complexes are relatively stable in aqueous solutions. HCl, on the other hand, is rarely employed alone, despite the fact that some basic silicate minerals can be completely or partially dissolved using this acid at high temperatures and pressure, [11,12]. Another commonly used acid for sample breakdown is sulfuric acid (H$_2$SO$_4$). Its high boiling point contributes to its effectiveness (about 340°C). H$_2$SO$_4$ can dissolve oxides, hydroxides, carbonates, and sulfide ores [13].
4. Conclusion
From the research that has been done, it can be concluded that on average metals and rare earth metals are more dissolved in HNO₃ while for a mixture of acids, namely the use of H₂SO₄-HNO₃.

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Acknowledgement
The researchers would like thank to LPPM Bangka Belitung University for the financial support through the PDTJ scheme, RKAKL FT for the publication of this paper and to PT. Timah, Tbk in the analysis activities.