Selective Extraction of Metals from Pacific Sea Nodules with Dissolved Sulfur Dioxide

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SUMMARY

How to tritrate a rock? ... The following article illustrates the possibility of titrating a metallic constituent in a mineral with a selective reagent to an endpoint of near complete metal extraction. A very rapid and efficient—almost instantaneous and quantitative—method has been devised to differentially leach manganese, nickel, and cobalt to the exclusion of copper and iron from deep-sea nodules. In this method, a given weight of raw sea nodules ground to -200 mesh in an aqueous slurry is contacted for 10 min at room temperature and ambient pressure with a specified quantity of \( \text{SO}_2 \). An independent leaching parameter \( R \) has been defined as the ratio of the number of moles of \( \text{SO}_2 \) in the leaching solution to the weight of sea nodules. Variation of metal extraction with \( R \) generates sigmoidal curves characteristic of the metals extracted. A threshold value of \( R \) is required to initiate the leaching of a given metal from the mixed oxides. Once this threshold is reached, the metal recovery can rise above 95% in less than 10 minutes. For increasing value of \( R \) the extractability of various metals from Pacific sea nodules by \( \text{SO}_2 \) follows the order: Mn > Ni > Co > Fe, Al, Cu. Disparity in the \( R \) values permits a variety of selective leaching systems and metal separations simply by changing the quantity of \( \text{SO}_2 \) in the contacting solution. Success in this leaching system depends on the access of the nodule to less than 100 mesh. Above this critical size, leaching is slowed due to the inaccessibility of the inner particle reacting groups to the \( \text{SO}_2 \) leaching agent, resulting in lower and nonselective extractions of preferred metal values.

Leaching with HCl solutions of the same pH level as dissolved \( \text{SO}_2 \) yielded mixed, slow, and incomplete metal extractions. This finding rules out any interpretation based on hydrogen ion from the ionization of sulfurous acid as the leaching agent. The leaching curves observed in the new system resemble the complexometric titration curves of heavy metals with specific coordination species.

INTRODUCTION

The mineral resources of the ocean floor are abundant, but difficult to mine. To compensate for the high cost of offshore mining, mineral processing must adopt low-cost techniques to recover the metal values at prices competitive with on-shore traditional mining/metallurgical routes. The process discussed in this paper attempts to achieve this compensation: it is a simple, direct, nonroasting technique for metal recovery. The leaching agent, sulfur dioxide, is found to be very efficient and exceptionally fast in solubilizing certain metals from their hydrous oxide ores.

Sea nodules are commonly classified as either siliceous or calcareous, depending on whether the major gangue constituent is silica or a combination of calcium, magnesium, and carbonate. Nodules from the Atlantic Ocean are of both types and are relatively lower grade than the siliceous nodules of the Pacific Ocean. This paper deals only with the leaching characteristics of Pacific nodules whose lime content is not high enough to counteract the valuable attributes of \( \text{SO}_2 \) as a leaching agent. A subsequent paper will deal with the calcareous nodules, specifically, how reducing their lime content by a pretreatment step can significantly enhance the selectivity of metal extractions with dissolved \( \text{SO}_2 \).

Traditional methods of processing sea nodules involve a pyrometallurgical scheme which produces a Ni-Cu-Co-Mo-Fe-Mn alloy by smelting the nodules with coke in an electric furnace. Subsequent metal separation of the six-component alloy is obviously a difficult task.

Agarwal suggested a method wherein \( \text{NO}_2 \) or \( \text{SO}_2 \) is bubbled through a slurry of a specific type of nodule containing Cu and Ni in the manganese phase and Co in the iron phase. He suggested differential leaching to remove Mn, Ni, and Cu from a residue containing Fe and Co, but gave no data or examples to document or validate these ideas. Brooks and Martin reported extractions of 97% or more of the Mn, Ni, Co, and Cu, and 72% of the Fe by bubbling \( \text{SO}_2 \) into ore slurried with water. Zeitlin et al. obtained similar results from the interaction of \( \text{SO}_2 \) with Pacific ferromanganese nodules. The high iron extractions in the work of Brooks and Martin and Zeitlin wasted excessive amounts of sulfur dioxide and formed a troublesome impurity that complicated recovery of desirable metals in subsequent operations. Apparently, an uncontrolled treatment with \( \text{SO}_2 \) caused reversion to a stage approaching the "primordial soup" in the nodule protogenesis by indiscriminately dissolving everything.

Faugeras bubbled \( \text{SO}_2 \) in a slurry of sea nodules and then used sulfuric acid to form water-soluble sulfates of Mn, Ni, Cu, and Co. More recently, Agarwal used carbon monoxide at atmospheric pressure to catalytically reduce the ore in a water slurry at 50°C. The reduced ore was then subjected to ammoniacal leaching.

EXPERIMENTAL

A 50-lb random sample from a half-ton batch of Pacific sea nodules was ground to -200 mesh and blended. Chemical analysis of this head sample gave (wt.%): 5.7 Fe, 21.6 Mn, 3.5 Al, 1.8 Mg, 2.4 Ca, 9.3 Si, 0.87 Cu, 0.93 Ni, 0.20 Co, 0.05 S, and 0.70 \( \text{SO}_2 \).

A typical experiment to investigate the effect of the relative quantity of \( \text{SO}_2 \) in the leach solution on metal extraction involved reacting 20 g of the head sample with 200 ml of leach solution in a stoppered glass flask for 10 min at ambient temperature and pressure. The leach solutions were prepared by diluting to 200 ml various volumes of commercial "sulfurous acid" containing a certified percentage of \( \text{SO}_2 \). Similar experiments were performed to investigate the effect of time on metal extraction; in these experiments, however, the \( \text{SO}_2 \) content of the leaching solution was kept constant while the duration of each leaching test was varied.
To study the effect of nodule particle size on metal extraction, a 2-kg random sample of the half-ton batch of nodules was comminuted to -6 mesh with a steel mortar and pestle and then screened to give -6 + 12, -12 + 20, -20 + 28, -28 + 50, -50 + 100, and -100 mesh fractions. Each size fraction was blended and chemically analyzed. Table I shows weight percent and partial chemical analysis for each size fraction. The chemical analysis of the -200 mesh head sample is included for comparison. For these tests, 20 g of each size fraction and the -200 mesh head sample were slurried with 200 ml of leach solution containing 5.9% SO$_2$ in stoppered glass flasks for 10 min at ambient pressure and temperature.

To study the effect of solution pH on metal extraction, 20 g of the head sample (-200 mesh) were reacted for 10 min with 200 ml of 7.4% aqueous SO$_2$ and with other leaching solutions prepared by diluting this solution with 100,- 200, and 300 ml of distilled water. The pH of these four solutions was 1.18, 1.23, 1.55, and 1.60 respectively. Also, 20 g of the head sample were reacted for 10 min with 200 ml of hydrochloric acid solutions of pH 0.97, 1.13, 1.21, 1.35, 1.70, and 1.75 respectively.

At the completion of each leaching test the slurries were filtered and the residues washed with distilled water. Except for leaching with HCl, the filtrate in the rest of the experiments was virtually colorless. The residues were dried, weighed, and analyzed for Ni, Co, Cu, Mn, Fe, Al, Ca, and Mg by atomic absorption spectroscopy. Percent metal recovery (or solubilization from the nodules) was calculated from the difference in weight and analyses of the head samples and the residues after these leaching tests were completed.

### RESULTS AND DISCUSSION

Although many investigators have attempted leaching with sulfurous acid (sometimes by bubbling SO$_2$ into an ore slurry) they did not encounter the high recoveries and selectivities observed in this work. In previous research, leaching was conducted with an overabundance of SO$_2$ for prolonged periods of time, and oxygen was sometimes added as a prelude to forming sulfuric acid. This resulted in partial and nonselective extractions and, often, in the formation of slimes. The results of our research, on the other hand, indicate that limiting leaching time and concentration of SO$_2$ is more effective in achieving higher and selective metal recoveries.

Experiments in this investigation were therefore designed to study the effects of relative concentration of SO$_2$, leaching time, ore particle size, and solution pH. The results revealed some basic mechanisms that help define the conditions required to achieve success in leaching with SO$_2$.

<table>
<thead>
<tr>
<th>Size Fraction, Mesh*</th>
<th>Fraction of Total, Wt.%</th>
<th>Composition, Wt.%</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
<th>Ni</th>
<th>Co</th>
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<tbody>
<tr>
<td>-6 + 12</td>
<td>38.9</td>
<td></td>
<td>22.7</td>
<td>5.8</td>
<td>0.86</td>
<td>1.09</td>
<td>0.22</td>
</tr>
<tr>
<td>-12 + 20</td>
<td>32.5</td>
<td></td>
<td>22.8</td>
<td>5.9</td>
<td>0.82</td>
<td>1.09</td>
<td>0.23</td>
</tr>
<tr>
<td>-20 + 28</td>
<td>6.8</td>
<td></td>
<td>22.8</td>
<td>6.0</td>
<td>0.87</td>
<td>1.06</td>
<td>0.23</td>
</tr>
<tr>
<td>-28 + 50</td>
<td>7.3</td>
<td></td>
<td>23.8</td>
<td>5.5</td>
<td>0.91</td>
<td>1.12</td>
<td>0.22</td>
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<tr>
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<td></td>
<td>23.0</td>
<td>6.1</td>
<td>0.85</td>
<td>1.06</td>
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<tr>
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<td>21.1</td>
<td>6.1</td>
<td>0.80</td>
<td>0.93</td>
<td>0.23</td>
</tr>
<tr>
<td>-200 **</td>
<td>21.6</td>
<td></td>
<td>5.7</td>
<td>0.87</td>
<td>0.93</td>
<td>0.20</td>
<td></td>
</tr>
</tbody>
</table>

*U.S. Standard screen sizes ** -200 mesh head sample

![Figure 1. Leaching curves (10 min) for several metal values from 20 g of -200 mesh nodules in water containing various quantities of SO$_2$.](image-url)