Column simulation of Fe, Ti, V heap leaching from titanomagnetite ore

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Abstract. The results of the research of the process of metals extraction from titanomagnetite ore are presented. The experiments were conducted in PVC columns. The most efficient metal recovery is achieved at a hydrofluoric acid concentration of 4 mol/L and ammonium fluoride concentration of 0.42 mol/L. This represents approximately 10% for titanium, iron and vanadium. Selectivity on titanium during percolation of a solution with a hydrofluoric acid concentration of 1 mol/L and ammonium fluoride of 2.5 mol/L is observed.

1. Introduction
Deposits of titanomagnetite ores are considered as one of the promising industrial sources of iron ore, vanadium, titanium and other valuable elements [1]. For example, the Chineisk complex deposit of vanadium-containing titanomagnetites (Northern Transbaikal area, Russia) is one of the largest deposits in the world in terms of ore stocks (approximately 30 billion tons) [2].

Hydrometallurgical technologies for processing titanomagnetite ores are divided into acid and alkaline methods. Acidic processing methods are based on the dissolution of iron (II, III), vanadium and partially titanium (IV) and their transfer to the liquid phase with subsequent separation operations (precipitation, extraction). In the process of hydrochloric acid decomposition of ore, iron, vanadium, manganese pass into the solution, but titanium and silicon remain in the precipitate. The degree of ore decomposition essentially depends on the concentration and consumption of reagents, temperature conditions and the duration of the process. However, the known hydrometallurgical methods of processing of titanomagnetite ores have disadvantages such as multistage and high energy costs. Therefore, the development of cost-effective titanomagnetite ore processing technology is an important and urgent scientific and technical problem [1,3–5].

Heap leaching is well-established as a relatively low-cost and low-energy method of extracting metals (Au, Cu, U) from low grade ores, but it is practically not used for the processing of titanomagnetite ores[6].

Particular interest are hydrometallurgical technologies for ore processing, based on the effect of solutions containing ammonium and fluorine ions on the mineral material. The basis of the ore processing is that the oxides of transition and non-transition elements in contact with ammonium fluoride or solutions of ammonium fluoride and hydrofluoric acid form fluorometallates or oxofluorometallates favorable for further processing [7,8].

2. Experimental part

2.1 Ore
In the current work, we used a titanomagnetite ore from the Chineisk deposit (Chita region). The
average particle diameter in the ore was approximately 20 mm (the ore was provided by public
corporation Zabaikalstalinvest, Novaya Chara, Russia).

2.2 Leaching tests
The process of Ti, V and Fe leaching from the ore was simulated in PVC columns. The experiments
were conducted in PVC columns with a height of 1 m and a diameter of 100 mm. Four parallel
experiments were conducted with different leach aqueous solutions of ammonium fluoride and
hydrofluoric acid. 15 kg of ore were added in each column. The volume of leach solution was 15 liters
for each column and irrigation density was 250 ml/h. The percolation process was carried out in the
circulation mode. The leach solutions were recycled four times and the fifth cycle was carried out with
freshly prepared solutions. Samples of solutions were taken to analyze the content of Ti, Fe and V after
each cycle. The column experimental conditions are presented in table 1.

Table 1. Column experimental conditions.

| Column number | 1  | 2  | 3  | 4  |
|---------------|----|----|----|----|
| HF (mol/L)    | 4  | 1  | 1  | 1  |
| NH₄F (mol/L)  | 0.5| 2.5| 0.5| 1  |
| Temperature (°C) | 20 |    |    |    |
| Irrigation density (ml/h) | 250 |    |    |    |
| Sample weight (kg) | 15 |    |    |    |
| Leach solutions volume (L) | 15 |    |    |    |

2.3 Use of analytical techniques
The titanium, vanadium and iron concentration in the solution, and the elemental composition of the ore
were determined using inductively coupled plasma mass spectrometry on a mass spectrometer ICP-MS
ELAN-9000 DRC-e (Perkin Elmer USA).

3. Results and discussion

3.1 Characterization of the ore
According to the results of elemental analysis, the sample of titanomagnetite ore contains: Fe – 55.00
wt %, Ti – 6.84 wt %, V – 0.48 wt %. Table 2 reveals that the ore from the Chineisk deposit contains:
aluminum (2.08 wt.%), manganese (0.21 wt.%), nickel (0.024 wt.%), tin (0.040 wt.%), chromium (0.011
wt.%), silicon (0.78 wt.%), copper (0.038 wt.%), zirconium (0.0024% wt.), strontium (0.0031 wt.%),
scandium (0.0021 wt.%), gallium (0.0039 wt.%).

Table 2. The elemental composition of the ore (ICP).

| Element | Mass Fraction (wt %) | Element | Mass Fraction (wt %) | Element | Mass Fraction (wt %) |
|---------|----------------------|---------|----------------------|---------|----------------------|
| Fe      | 55.0                 | Al      | 2.08                 | Mn      | 0.21                 |
| Ti      | 6.84                 | Ni      | 0.024                | Ga      | 0.0039               |
| V       | 0.48                 | Sn      | 0.040                | Zr      | 0.0024               |
| Si      | 0.78                 | Cu      | 0.038                | Sc      | 0.0021               |
| Cr      | 0.011                | Sr      | 0.0031               | Sb      | 0.0029               |

Thus, the titanomagnetite ore of the Chineisk deposit has a high titanium and vanadium content (V₂O₅
0.8-1.0 wt.%, TiO₂ 11-12 wt.%) and can be considered as a huge resource for obtaining vanadium iron
and titanium dioxide. However, the pyrometallurgical processing of such ore will be difficult due to the
high content of TiO$_2$ (>4%). The relatively high content of some non-ferrous and rare metals makes it possible to extract them.

3.2 Leaching efficiency

This section presents the results of studying column simulation of Fe, Ti, V heap leaching from titanomagnetite ore.

The results of the experiments are presented in the table and diagrams: extraction efficiency of Ti, V, Fe in column 1 and column 2 (figure 1) and extraction efficiency of Ti, V, Fe in column 3 and column 4 (figure 2).

Table 3. Comparative results obtained after leaching of titanomagnetite ore from the Chineisk deposit.

| Column no. | The content in the solution after four cycles of percolation (g/L) | Extraction of metals into the solution after 4 cycles of percolation (%) | Extraction of metals into the solution after the 5th cycle of percolation (%) |
|-----------|---------------------------------------------------------------|-------------------------------------------------|------------------------------------------|
|           | Ti     | V       | Fe      | Ti     | V       | Fe      | Ti     | V       | Fe      |
| 1         | 4.46   | 0.35    | 41.95   | 6.52   | 7.29    | 7.63    | 10.90  | 11.29   | 9.99    |
| 2         | 0.65   | 0.01    | 0.45    | 0.95   | 0.23    | 0.08    | 1.26   | 0.17    | 0.12    |
| 3         | 0.71   | 0.08    | 10.70   | 1.04   | 1.69    | 1.94    | 1.05   | 2.15    | 1.99    |
| 4         | 1.35   | 0.14    | 12.69   | 1.98   | 2.92    | 2.31    | 1.35   | 2.33    | 1.78    |

As follows from the table and diagram (figure 1 (a)), the highest degree of extraction of metals from the ore is achieved in column No. 1, where the concentration of HF is 4 mol/L and NH$_4$F is 0.5 mol/L. Thus, after 4 cycles of percolation, extraction to solution is 6.52 % Ti, 7.29 % V and 7.63 % Fe. After the fifth percolation cycle with a freshly prepared solution, these values are 10.90 %, 11.29 %, and 9.99 % respectively. Therefore, ore is most efficiently processed using repeated percolation of solution No. 1.

![Figure 1](image1.png)

**Figure 1.** Extraction efficiency of Ti, V, Fe in column 1 (a) and column 2 (b).

In column No. 2, when using a solution with a concentration of HF - 1 mol/L and NH$_4$F - 2.5 mol/L, a low degree of metals extraction is observed, however, the content of titanium predominates in the enriched process solution (figure 1 (b)). The degree of extraction in the solution is: Ti - 1.26 %, V - 0.17 %, and Fe - 0.12 %. Thus, with repeated percolation of solution No. 2, the method allows to achieve the selective extraction of titanium and the enrichment of titanomagnetite ore with iron and vanadium.
A low degree of extraction of metals is observed in columns No. 3 and No. 4; moreover, there is no selectivity on one of the elements. (figure 2 (a), (b)).

![Figure 2](image)

**Figure 2.** Extraction efficiency of Ti, V, Fe in column 3 (a) and column 4 (b).

4. **Conclusion**

This study confirms the potential of heap leaching of titanomagnetite ore for the extraction of Ti, V and Fe. The titanomagnetite ore of the Chineisk deposit contains Fe – 55.00 wt %, Ti – 6.84 wt %, V – 0.48 wt % and can be considered as a huge resource for obtaining vanadium, iron and titanium dioxide. Experimental results show that the most effective extraction of ore components is achieved at a concentration of hydrofluoric acid - 4 mol/L and ammonium fluoride - 0.5 mol/L and is approximately 10% for titanium, iron and vanadium. Selective extraction of titanium is observed during percolation of a solution with a concentration of hydrofluoric acid of 1 mol/L and ammonium fluoride 2.5 mol/L.

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