Mineralogy and process properties of Kolvitsky titanomagnetite ore

YuN Neradovsky¹, SA Alekseeva²* and EV Chernousenko²

¹Geological Institute, Kola Science Center, Russian Academy of Sciences, Apatity, Russia
²Mining Institute, Kola Science Center, Russian Academy of Sciences, Apatity, Russia

E-mail: *alekseeva@goi.kolasc.net.ru

Abstract. The authors study material composition, texture and structure, as well as process properties of titanomagnetite or from Kolvitsky deposit on the Kola Peninsula. It is found that the ore posses high potential as a unique combination of iron, titanium, vanadium, ilmenite, copper–nickel sulphides and platinum. Pre-treatment of lump material by magnetic separation allows obtaining iron-free nonmagnetic fraction after intermediate crushing. The methods of magnetic, flotation and gravity separation are discussed. The article demonstrates feasibility of integrated processing of this type with production of titanomagnetite, sulphide and ilmenite concentrates for the ferrous and nonferrous metallurgy.

1. Introduction

Global consumption of metals increases, and it is required to enlarge supply of metallurgy with raw materials. Alongside with conventional metal ore, complex ore can become an important resource component for metallurgy in the world and in Russia. Titanomagnetite ore widely spread in the world belong to complex ore. This ore contains iron and titanium, and their commercial value is raised by the presence of vanadium, which is one of the main components of this ore. Moreover, some complex ore deposits contain recoverable copper, cobalt, nickel, gold, platinum, etc. [1, 2].

Shining examples of titanomagnetite ore production and commercial use abroad are deposits of the Bushveld Complex in South Africa, Lac Tio in Canada, Panzhihua in China, etc. Russia holds considerable reserves of this type ore, in amount of round 50% of all global reserves. All in all in the territory of Russia, more than 40 titanomagnetite deposits are explored and appraised (Ural, Siberia, Far East, Karelia, Kola Peninsula). The Kola Peninsula, solely, accommodates more than 10 deposits of titanomagnetite ore [3–8].

Commercial development of titanomagnetite ore is restricted by high mass percent of titanium dioxide in produced iron–vanadium concentrate. Currently, Russian metallurgy uses only low-titanium ore with TiO₂ content not higher than 4% (Gusevogosrsk deposit, Ural). Titanomagnetite with TiO₂ content higher than 5–8% can only be smelted in electrical furnaces, which produce refractory titanian slug needing higher temperature of treatment. Regarding processing technologies for high-titanium titanomagnetite, for instance, in South Africa, raw material (up to 18% of TiO₂) is pre-roasted in a rotating tilted furnace and then is subjected to electrical smelting [9, 10].

Among the Kola deposits, only three fields are low-titanium ore and occur in the hard-to-reach Keivy area, although they can be extracted as infrastructure is developed in the north-east of the Kola Peninsula.
Other Kola deposits are medium-titanium ore or magnetic titanium–vanadium ore: Gremyakha-Vyrmes, Tsaginsky, Kolvitsky, Tsentralny and other. These deposits are better explored and occur in developed areas with mature communication network, or the development is in process. For medium-titanium ore, the Kola Science Center has developed a technology for processing titanomagnetite concentrate by pyrometallurgical method with production of powdered iron, sodium titanate, titanium vanadate and titanium nitride; moreover, chemical composition of feed stock for this method is of no importance, and lab tests of Kolvitsky, Gremyakha-Vyrmes and Khibiny titanomagnetite produce positive results [11, 12].

Kolvitsky ore is a promising source of titanomagnetite on the Kola Peninsula. The deposit occurs in the south of the Murmansk Region, 50 km eastward of Kandalaksha. The ore possesses high complex potential as a unique combination of magnetic titanium–vanadium–ilmenite ore with content of copper–nickel sulphides and low-sulphide platinum. Probable reserves of this ore make 100 Mt at the average content of Fe₂O₃ 40%, TiO₂ 7% and V₂O₅ 0.2% [12].

2. Research objects and methods
The tests were carried out on a titanomagnetite sample 450 kg in weight, taken in the detail exploration site of Kolvitsky deposit. The sample is rich in titanomagnetite, and is represented by cores and lumps of densely disseminated and massive ore. Mineral composition of ore, %: titanomagnetite—75–93, ilmenite—to 20, spinel—to 5; sulphides—1–5. Chemical composition (main components), %: Fe₆O₇—51, FeO—32.2, Fe₂O₃—37.2, TiO₂—11.1, Cu—0.124, Ni—0.07, S—0.25, V₂O₅—0.5, noble metals—0.806 g/t, platinum group elements—0.012 g/t.

Mineralogy and process properties of the ore was analyzed using a package of methods, including, microscopic, spectral, chemical, grain-size and magnetometric analyses.

The technological studies involved magnetic, flotation and gravity separation. Ore milling used rod and ball mills 30 and 15 l in capacity, respectively. Magnetic separation was implemented on wet magnetic separator 120-T and dry and electric magnetic separator 138-T. Flotation tests were run on lab machines 237 FL and 135-D-FL. Gravity separation was carried out on enlarged lab pant with spiral separators VSR-500 and concentration tables SKO-0.5.

3. Material constitution of ore
Titanomagnetite ore occurs in clinopyroxene and wehrlite, has laminated structure and massive dissemination. By the titanomagnetite content, there is division into low-grade (30%), medium grade (30–50%), high-grade disseminated (50–80%) and massive (>80%) ore (see Figure 1). The basic minerals are titanomagnetite—42–77%, ilmenite—4–10% and spinel—3–12% [13].

![Figure 1. Kolvitsky titanomagnetite ore structure: (a) medium-grade ore; (b) high-grade disseminated ore; (c) massive ore. Reflected light image (TiMt—titanomagnetite; Ilm—ilmenite; Spl—spinel;Slf—sulphides).](image-url)

Titanomagnetite is represented by a complex four-component system: matrix, ulvospinel, spinel and ilmenite, formed as a result of double disintegration of solid solution. The disintegration products make two persistent paragenesis forms: spinel–ulvospinel and spine–ulmenite. In the first stage, as a
Consequence of temperature decrease, spinel–ulvospinel (Spl + Usp) evolves with the content of 31.9% Spl and 68.1% Usp. This paragenesis form makes 35.5% of titanomagnetite volume. In the second stage, under influence of tectonic deformation, spinel–ilmenite (Spl + Ilm) evolves with the content of 37% Spl and 63% Ilm. This paragenesis form makes 18.5% in the volume of titanomagnetite. During disintegration of solid solution, vanadium and ulvospinel migrate. Later on, at the stage of ilmenite separation, vanadium remains in the matrix of titanomagnetite. As a result, two phases rich with vanadium form: titanomagnetite matrix and ulvospinel.

Thus, processing of ore can produce magnetic titanium–vanadium (magnetite–ulvospinel) and magnetic titanium(ilmite) products [14].

Copper–nickel sulphides are present in rocks and titanomagnetite ore in the form of dissemination at 5–10%. The dissemination mainly concentrates beyond titanomagnetite and, in connection with this, the content of Cu, Ni and S is 0.232, 0.098 and 0.35% in enclosing rocks and 0.168, 0.075 and 0.36% in titanomagnetite ore, respectively. Sulphides are separated from titanomagnetite in ore, more developed in the layers of disseminate ore and less developed in massive ore (see Figure 1). There are 13 mineral phases sulphides, with predominant copper phase. The base minerals are troilite, chalcopyrite, cubanite and pentlandite; the secondary minerals are bornite, chalcocite, covelline, makinavite, violarite, etc.

Platinum group elements are Pd, Pt and Rh at the content from 0.020 to 0.814 g/t in rocks and from 0.004 to 0.036 g/t in titanomagnetite ore. The content of Au and Ag is high. For instance, the silver content ranges from 0.56 to 1.32 g/t in rocks and from 0.52 to 1.03 g/t in titanomagnetite ore. The total content of platinum group elements, Au and Ag reaches 1.7 g/t in rocks with the sulphide dissemination. It is observed that the contents of platinum group elements, Au and Ag correlate with the content of Cu.

Grains of noble metals vary from 0.2 to 20 μm in size. It is found that noble metals are mostly represented by tellurium–bismuthite of palladium and silver. From the analysis of mineral associations, 78% of noble metal grains are included in the primary sulphide minerals, chiefly in chalcopyrite and cubanite, while 22% of grains occur in streaks intersecting rock-forming silicates [13].

Thus, Kolvitsky titanomagnetite is assumed as the complex Fe–Ti–V–Ni–Cu ore.

4. Process properties of titanomagnetite ore

Processing of titanomagnetite ore uses most often combination of circuits [15–19]. The first stage is production of magnetic concentrate of dry or wet magnetic separation, the second stage is production of ilmenite, sulphide and other concentrates from the nonmagnetic fraction.

For the ore sample under analysis, feasibility of pretreatment of lump material was studied [2]. The method of processing was chosen to be magnetic separation as components of the ore have essentially different magnetic properties. The tests were carried out on lump material – 60 + 30 mm in size using magnetometric method based on measurement of magnetic sensitivity (χ, SI-system units). To this effect, portable susceptimeter SM-30 was used.

Table 1. Magnetometric separation data of the sample, %.

| χ, SI units | Yield | Content | Recovery |
|-------------|-------|---------|----------|
|             |       | Fe_{tot} | V_{2}O_{5} | TiO_{2} | Cu | Ni | S | Fe_{tot} | V_{2}O_{5} | TiO_{2} | Cu | Ni | S |
| 500–1000    | 51.99 | 55.21   | 0.61       | 12.12   | 0.116 | 0.073 | 0.25 | 56.26 | 52.91 | 56.98 | 46.96 | 54.39 | 51.39 |
| 200–500     | 33.31 | 51.61   | 0.64       | 11.20   | 0.132 | 0.067 | 0.27 | 33.70 | 35.38 | 33.77 | 34.10 | 31.80 | 35.88 |
| 0–200       | 6.52  | 14.94   | 0.34       | 1.53    | 0.244 | 0.068 | 0.24 | 1.91  | 3.66  | 0.91  | 12.34 | 6.32  | 6.24  |
| Total       | 91.82 | 51.04   | 0.60       | 11.03   | 0.131 | 0.071 | 0.26 | 91.86 | 91.95 | 91.65 | 93.40 | 92.51 | 93.51 |
| Size – 30 mm| 8.18  | 50.73   | 0.59       | 11.27   | 0.104 | 0.064 | 0.20 | 8.14  | 8.05  | 8.35  | 6.60  | 7.49  | 6.49  |
| Initial product | 100  | 51.02   | 0.60       | 11.05   | 0.129 | 0.070 | 0.25 | 100   | 100   | 100   | 100   | 100   | 100   |
By the results of magnetometric separation, three main fractions are distinguished in the sample (Table 1). The product of lumps with magnetic susceptibility higher than $500 \times 10^{-4}$ SI units mostly accumulate massive ore containing 75–95% of titanomagnetite and 0–20% of ilmenite. This product yield was 52%. By the content of $Fe_{\text{tot}}$, this product is not finished and needs processing.

The fraction of lumps with the magnetic susceptibility of 200–500$ \times 10^{-4}$ SI units is middlings; it combines low-grade and high-grade disseminated ore containing 35–75% of titanomagnetite and 0–20% of ilmenite. The yield of this product made 33%.

The fraction of the lumps having magnetic susceptibility of $200 \times 10^{-4}$ SI units holds enclosing rocks represented by pyroxinite, olivinite and crystal plagioclase–garnet–pyroxene shale. By the content of titanomagnetite and ilmenite (0–5%), this product can be assumed as tailings but the sulphide mineralization leaves the product in processing. Moreover, this is the smallest fraction, its yield was merely 6.5%, which was typical of the originally high-grade ore. Decision on advisability of the lump separation can be made after testing the commercial-type ore sample.

Thus, magnetic separation of lumps allows removal of fraction that is free from titanomagnetite and ilmenite. This fraction can be dumped, ore dressed separately if its yield is not less than 20–30%.

The lump size was chosen based on the studied kinetics of grinding and dissociation of base minerals. It is found that dissociation kinetics of ilmenite and titanomagnetite has some features. At the early stages of grinding, dissociation of limonite lags behind titanomagnetite. Free grains of titanomagnetite total 90% at grain size of 1.4 mm, while ilmenite reaches such percent when ground to 0.6 mm. The obtained results concord with the size of dissemination: dominating dissemination of titanomagnetite is 0.7–1.5 mm (can reach to 10 mm) while dissemination of ilmenite is 0.5–0.7 mm (to 3 mm). Stating from ground size 0.4 mm, titanomagnetite and ilmenite have almost the similarly high rate of dissociation, corresponding to 95–96% of their free grains. Assessment of dissociation of sulphides shows that dissociation of sulphides is not higher than 70–80% at the ground grain size of –0.4 mm and nearly 90% in the material with the grain size of –0.2 mm.

With regard to the dissociation results, the tests on dressing of size grades –0.4 and –0.2 mm were compared.

The wet magnetic separation data at the magnetic field strength of 900 E were alike. In both cases, titanomagnetite concentrate with the $Fe_{\text{tot}}$ content of 61–62% and recovery of 88–89% was produced. Larger size grinding to –0.6 mm failed to result in production of concentrate quality higher than 60% of $Fe_{\text{tot}}$. In this manner, the magnetic separation provides two products:

1. Highly magnetic magnetite–ulvospinel with the content of $Fe_{\text{tot}}$ 61–62%, $TiO_2$ 9.6% and $V_2O_3$ 0.54. This product holds around 75% of ore mass and is a complex source for production of iron, titanium and vanadium.

2. Nonmagnetic sulphide–ilmanite with the content of $TiO_2$ 12.5–13.5%, Ni 0.1%, $Cu$—0.28%, $S$ 0.5–0.6%, noble metals 0.72 g/t and platinum group elements 0.084 g/t. This product holds around 25% of ore mass and is a complex source for production of nickel, copper, cobalt, titanium and noble metals.

The next stage of preparation was processing of nonmagnetic product, production of sulphide and ilmenite concentrates is possible both with flotation and gravity separation. The research show that gravity methods are inefficient early in the nonmagnetic fraction processing circuit as they are unable to concentrate sulphides in one of the products, or to obtain products free of sulphides—they evenly spread out in all fractions. For this reason, the nonmagnetic fraction was immediately sent to sulphide flotation.

The flotation was carried out in an alkaline medium created by caustic ash. The collectors were butyl xanthate and Aeroflot, the frother was agent T-80 and the depressor of rock-forming minerals was carboxymethyl cellulose. The flotation modes were analyzed at the initial grain sizes of –0.4 and –0.2 mm. The size grades were selected with regard to sufficient dissociation of sulphides and producibility of ilmenite concentrate from gravity separation product. The best results were obtained with the size grade of –0.2 mm. The recovery of $Cu$, $Ni$ and $S$ in the rougher sulphide concentrate was 78.9, 61.1 and 79.6%, respectively, at the content of 1.9, 0.6 and 4.4%. The loss of sulphides in the
middlings is mainly owing to sporadic aggregates with silicates. After a cycle of recleaner flotation circuits, the content of Cu in concentrate raised to 4%, Ni—to 1.5% and S—to 11%, while noble metals and platinum group elements increased their cumulative content to 6.4 g/t. In addition, the concentration of ferrous metals (Cu, Ni) in froth product grew relative to initial feed (nonmagnetic fraction) 14 times. The concentration of noble metals increased, too: Ag—8 times; Au—6 times; Pt—3 times; Pd—6 times, Ru—1.5 times; Rh—2.5 times. Silver, gold and palladium are especially considerably concentrated.

For estimation of nonferrous metal recoverability in concentrate, the closed-circuit flotation tests were carried out with middlings to be returned in the circuit. In the closed circuit, at particle size of –0.2 mm, extraction of nonferrous metals in sulphide concentrate made 72% Cu and 71.4% Ni at contents of 4.1 and 1.7%, respectively.

A higher quality concentrate without reduction in recovery can be produced at the smaller size grade of grinding. This was confirmed by the mineralogical assessment of froth product obtained at the size grade of –0.2 mm: the concentrate contained aggregates of sulphides and silicates. In this case, with a view to producing ilmenite concentrate from tailings of sulphide flotation, dissociation of aggregates can be achieved with re-grinding of rougher sulphide concentrate or middlings.

Producibility of a higher quality concentrate was tested. At the ground size of –0.1 mm, the sulphide concentrate was obtained with the contents of Cu 8.6–11.5% and Ni 2.8–3.2%.

Ilmenite concentrate was produced using gravity methods, spiral separators and concentration tables. The gravity separation feed was the flotation middlings subjected to desliming before spiral separation. The spiral separator let out three products: concentrate, middlings and tailings. The tailings with the content of TiO₂ 5.6% were withdrawn from processing and dumped, while the concentrate ad middlings were separately sent to recleaning on concentration tables. Table 2 reports final data of the process.

| Product          | Yield   | Content of TiO₂ | Recovery of TiO₂ | Processing efficiency |
|------------------|---------|-----------------|------------------|----------------------|
| Gravity concentrate | 8.55     | 39.12           | 22.83            | 16.7                 |
| Middlings        | 18.36   | 22.80           | 28.59            | 12.0                 |
| Tailings         | 42.52   | 6.77            | 19.65            | –26.8                |
| Slime            | 30.57   | 13.86           | 28.93            | –1.9                 |
| Feed             | 100.00  | 14.65           | 100.00           | 0.0                  |

Recovery in the gravity concentrate made 22.8% of the feed at the content of TiO₂ 39.01%. The attempts to increase the yield had no success even after more recleaner flotation circuits. After every next recleaner, the yield and quality of the concentrated decreased. This is connected with the fact that in the middlings zone, particle with similar gravity properties accumulate: the product is represented by pyroxene by 60–70%, while pyroxene has similar gravity as ilmenite. Recovery of titanium dioxide in middlings exceeded 25%; accordingly, by handling the problem of dissociation of this product, it would be possible to improve essentially gravity separation efficiency. Aiming to refine gravity concentrate, electromagnetic separation can be used as it provides a product with the content of TiO₂ 42–45% at the magnetic field strength of 1800–3500 E.

At this stage, the research demonstrates producibility of ilmenite product. The studies should be continued on a commercial ore sample with a view to analyzing potential of gravity separation efficiency improvement and performance of other mineral processing methods, in particular, flotation.

5. Conclusions
Material constitution of titanomagnetite ore has been studied. Enclosing rocks are mostly pyroxene. The base minerals are titanomagnetite, ilmenite and spinel. Copper–nickel sulphides are present both in rocks and titanomagnetite ore as disseminations at the content of 5–10%. It is found that there 13
mineral phases of sulphides, including copper phases. Platinum group elements are Pb, Pt and Rh, Au and Ag show high contents, and total content of noble metals and platinum group elements reach 1.7 g/t. It is observed that the contents of platinum group elements, Au, Ag and Cu correlate.

It is shown that preliminary magnetic separation of lump ore materials allows obtaining nonmagnetic fraction after intermediate crushing.

As a result of mineralogical and technological research, titanomagnetite, sulphide and ilmenite concentrates have been produced.

The wet magnetic separation yields the titanomagnetite concentrate with the content of 61–62% Fe\textsubscript{tot}, 9.6% TiO\textsubscript{2} and 0.54% V\textsubscript{2}O\textsubscript{5}. Recovery of Fe\textsubscript{tot} makes 88–89%.

Different regimes of nonmagnetic product flotation are analyzed. Achievable recovery of ferrous metals in the concentrate in a closed circuit with the return of middlings back in the flotation scheme is assessed. At the size grade of –0.2 mm, the recovery of nonferrous metals in the sulphide concentrate made 72% Cu and 71.4% Ni (at the contents of 4.1 and 1.7%, respectively), while the content of noble metals and platinum group elements jointly grew to 6.4 g/t.

Productivity of a higher quality sulphide concentrate with the content of 8.6–11.5% of copper and 2.8–3.2% of nickel was examined at the reduced size grade to –0.1 mm.

Concentration ability of ilmenite by gravity methods is demonstrated. Using the spiral separation and concentration tables, a rougher concentrate with the content of 39.1% TiO\textsubscript{2} has been obtained. The electromagnetic separation can improve the concentrate quality up to the content of 42–45% TiO\textsubscript{2}.

Thus, the Kolvitsky titanomagnetite ore possesses high complex potential for production of suitable concentrates for the ferrous and nonferrous metallurgy.

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