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METAL-CONTAINING FRACTION OF VOLYN BASALTS

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Abstract. For the basalts of Volyn Polissia and the accompanying tuff and lava breccia rocks, studies by geologists and scientists of Ukraine have established unique properties regarding the content of valuable metals—non-ferrous, ferrous, precious, rare-earth. Copper was identified as the practically significant ore-forming element, but alongside it, for example, iron and silver are present in considerable quantities and in native form, so basalt deposits are often considered polymetallic. The main attention of researchers has been paid to copper, investigating its distribution in basalt deposits and extraction methods. A problem in the processing technologies being developed is the separation of metals from each other. Obviously, in the final processing cycle this is done by pyrometallurgical and hydrometallurgical methods, but at the ore preparation stage it is possible to use physical methods of electrical and magnetic separation. The development of physical processes for processing basalt raw materials is ongoing. In this regard, the purpose of the article is to analyze the iron-containing fraction in basalt rocks, which has been insufficiently studied so far. For the analysis, methods of spectroscopic and mineralogical analysis, dry magnetic separation of individual size classes of rocks were applied. It has been established that the iron-containing fraction is represented predominantly by iron, titanium, vanadium, and their quantities are several times higher than background values. The metal content is: in basalt up to 15.75% Fe, 2.4% Ti, 0.05% V (or 0.09% V_2O_5); in lava breccia up to 14.5% Fe, >0.7% Ti, 0.3% V (or 0.53% V_2O_5); in tuff up to 18.2–21.6% Fe, 2.63–2.18% Ti, 0.1% V (or 0.18% V_2O_5). Features of the mineralogical composition of the rocks include a small amount of copper and iron sulfides and sulfates, and the presence of natural copper-iron alloys. The magnetic component is represented by magnetite and titanomagnetite. Dry magnetic separation of the rocks was studied for feed size 2.5 + 0 mm at a magnetic field induction of 0.16 T. The copper content in the initial feed was: for basalt 2.62%, lava breccia 1.36%, tuff 0.53%. The yield of the magnetic fraction and the possibility of concentrating copper in the non-magnetic product were investigated. It was found that the magnetic concentrate yield from basalt is 55.16% of the sample, from lava breccia 38.13%, from tuff 40.03%. Copper recovery into the magnetic separation waste (non-magnetic fraction) is: for basalt 74.7%, for lava breccia 75.58%, for tuff 68.6%. The use of magnetic separation is expedient at the ore preparation stage. Promising directions for increasing copper recovery in the non-magnetic product are reducing the feed size and using wet magnetic separation instead of dry.

Keywords: basalt, tuff, lava breccia, magnetic separation.

1. Introduction

To obtain domestic copper in Ukraine, the most promising sources are the copper showings in the basalt deposits of Volyn Polissia. As of 2021, the state approach to developing these deposits consisted of issuing special permits for additional geological exploration and pilot testing for the richest deposits (Zalisy-Shmenky, Zhyrychi – underground mining; and Rafalivka quarry – open-pit mining), as well as the Prutivskyi occurrence where the ores are copper-nickel sulfides. Relevant directives were given to the State Service of Geology and Mineral Resources of Ukraine and the state enterprise “Ukrainian State Geological Exploration Institute.” Currently, private enterprises such as PJSC “Rafalivka Quarry,” OJSC “Berestovets Special Quarry,” LLC “Klesiv Quarry of Nonmetallic Minerals Tekhnobud,” and others extract basalts as construction raw materials in the form of stone, crushed stone, basalt chips, screenings, and block stone for processing. Meanwhile, the basalt deposits of Volyn Polissia can confidently be classified as industrial oxide-native copper ores, with average grades of 1–2% Cu and low grades of 0.2–0.5% Cu [1–3].

The copper-bearing Volyn basalts are a unique copper-bearing raw material, and worldwide experience in processing them is very limited. The only analogous deposit

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in the Lake Superior region of the USA is now practically exhausted; the main technology used there was flotation. At present, work on copper extraction from Volyn basalts is being carried out jointly at M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine (IGTM of the NAS of Ukraine) and the National University of Water and Environmental Engineering. Significant contributions have been made by Academician Bulat A.F., Professors Nadutyi V.P., Malanchuk Z.R., and other scientists.

In addition to copper, basalt deposits are rich in other valuable metals, whose content significantly exceeds background levels [4]. In particular, there is a significant presence of iron-containing minerals in basalt deposits [4–6], but this issue has not been sufficiently studied. When processing the raw material, the challenge arises in separating the metals from each other. For example, when employing a typical copper flotation scheme, there arises a question whether additional pyrite or iron flotation should be performed, or whether magnetic separation should be used during ore preparation prior to copper extraction. Thus, studying the iron-containing fraction of basalt deposits is relevant and requires detailed investigation.

The aim of this work is to investigate the specifics of the iron-containing component of basalts and associated rocks - lava breccias (15–20%) and tuffs (10–15%) - as well as to study the performance indicators of magnetic separation of these rocks, namely, determining the quantity of the magnetic fraction obtainable and identifying the peculiarities of copper recovery into the non-magnetic product.

2. Methods

In this work, methods of spectroscopic analysis, mineralogical analysis, granulometric analysis, dry magnetic separation at a magnetic field induction of 0.16 T, and methods of mathematical and statistical processing of experiments were used.

3. Results and discussion

3.1 Using spectroscopic analysis methods, the content of iron, titanium, and vanadium was investigated in basalts, and then in lava breccias and tuffs (the associated rocks of basalt deposits). [4].

It was found that basalts from different quarries contain significant amounts of these metals (Table 1).

Lava breccia is a component of basalt deposits, comprising about 20%. Compared to basalts, lava breccias have a higher content of vanadium, copper, and silver (Table 2).

Volyn tuffs are divided into red and gray varieties; in basalt deposits, mostly red tuffs are present (in about 10% of the deposit). The metal content in tuffs is given in Table 3.

From the data in Tables 1–3, the following conclusions can be made:

- The iron content is highest in tuffs, up to 18.2–21.6% Fe; in basalts up to 15.75%; in lava breccia up to 14.5%.
- The titanium content is greatest in tuffs, up to 2.63–2.18%; in basalts up to 2.4%; in lava breccia (in one quarry) more than 0.7%;

- The vanadium content is highest in lava breccia – up to 0.3% V; in tuffs up to 0.1%; in basalts up to 0.05%. In terms of vanadium pentoxide, the V_2O_5 content in lava breccia is 0.53%, in tuff 0.18%, in basalt 0.09%. These data meet industrial requirements. For example, the titanomagnetite ores of the Kachkanar Mining and Processing Plant contain 14–15% Fe and 0.12–0.14% V_2O_5, and they are processed by a traditional magnetic scheme. Table 4 presents the background content of metals in the Earth's crust.

Table 1 – Content of metals in basalts of Volyn quarries*

Elements	Village: Khodosy, Hubyn, Midsk	Village: Berestovets, Yanova Dolyna (quarry No.2)	Village Ivanchi, Rafalivka quarry
Metals, %			
Fe	9.25	10.62	15.75
Ti	1.52	1.7	1.3 – 2.4
V	0.03	0.05	0.03
Cu	1.0	0.17	0.24–1.0
Oxides, % [4]			
Fe_2O_3+ FeO	6.03+6.46	3.36+10.63	5.5+15.3
TiO_2	2.54	2.85	2.2–4.0
V_2O_5	0.053	0.09	0.054
CuO	1.2	0.22	0.3–1.2
MnO_2	0.4	0.21	0.4

*Recalculation of oxides to metals: Fe_2O_3 contains70% Fe; FeO – 77.78% Fe; TiO_2 -59.93% Ti; V_2O_5 -56.01% V.

Table 2 – Content of metals in the lava breccia of the Rafalivka quarry

Metals	Content, %
Fe	10–14.5
Ti	>0.7
V	0.3
Cu	1.0–5.0
Mn	0.1
Ag, (g/t)	30–50

Table 3 – Content of metals in tuffs ,%

Red and gray tuffs		Metal 18.2/21.6 Fe_2O_3=26.0/32.25	Titanium 2.63/2.18 TiO_2=4.388/3.64	Cu 0.56/0.16
Metal	Tuffs from various quarries			
	Rafalivka	Berestovets	Yanova Dolyna	Near Tsvitoha River (Slavuta)
Fe	>7.0	15.0	>7.0	>1.0
Ti	>1.0	>1.0	0.5	0.7–1.0
V	0.015–0.03	0.1	0.03	0.03
Mn	0.05–0.1	0.1	0.07	0.07
Cu	0.02–0.3	0.05	>1.0	0.05

Table 4 – Background content of metals in the Earth's crust, %

Fe	5.63
Ti	0.565
V	0.012
Cu	0.006
Ag	0.0000075

Comparison of the data from Table 4 with those of Tables 1–3 shows that the basalt deposits have iron, titanium, and vanadium contents several times higher than the background values.

The question of industrial extraction of iron from basalts, as such, has not been considered; it is obvious that extracting titanium and especially vanadium is more attractive and economically beneficial.

It is known that in world practice ~88% of vanadium is produced from vanadium titanomagnetite. In fact, this is a mineral in which, in the magnetite (Fe_3O_4) lattice, trivalent iron is sometimes replaced by trivalent vanadium or trivalent titanium. Since basaltic rocks have pronounced magnetic properties, one should assume that they contain a significant amount of magnetite.

Considering the possibility of substituting trivalent iron with titanium or vanadium, the Fe-Ti-V mineral complex should be regarded as a unified triad when developing a comprehensive processing technology. At the stage of ore preparation and flotation, it is advisable to extract this complex together, and then carry out separation into individual metals by hydrometallurgical or pyrometallurgical methods.

3.2 Investigation of mineral composition. Depending on the mineral form in which iron is present in the rock, the rock may exhibit magnetic or non-magnetic properties. According to the research of Nadutyi V.P., Malanchuk E.Z. and other scientists, basalt, tuff, and lava breccia have significant magnetic properties [6–8]. This means that strongly magnetic minerals are present in the rocks, which was confirmed by mineralogical analysis (Table 5).

A microscopic analysis of particles of rocks of various sizes showed the presence of metallic conglomerates in the form of alloys of copper and iron, iron and silver, iron and ilmenite, etc.

Table 5 – Minerals of basaltic rocks

Non-magnetic and weakly magnetic minerals	Strongly magnetic minerals
- wüstite (FeO), limonite, hematite, goethit - complex metal oxides $MeO \cdot Fe_2O$; - natural alloys of iron with copper, iron with silver (with similar contents of these metals), natural brass (Cu-Zn) and bronze (Cu-Sn), multi-component alloys (Fe−Zn-Pb), (Zn−Fe−Ni−Cu), (Cu−Ni−Fe−Zn) In small quantity: - copper and iron sulfides: pyrite FeS, II (Fe_3S_4), III (Fe_2S_3), chalcopyrite $CuFeS_2$, bornite Cu_5FeS_4; - iron and copper sulfates (salts of sulfuric acid); -other derivatives of iron-containing minerals, e.g., iron potassium sulfide $KFeS_2$.	- magnetite$FeO \cdot Fe_2O_3$; -titanomagnetite $FeTiO_3 \cdot Fe_3O_4$; -pyrrhotite FeS_2 in small quantity

Investigations by Academician Lukin O.Yu. and Melnichuk V.G. [9] have proven that: “Unlike the macro-disseminations of native copper (films, streaks, nuggets), its micro-particles always contain Fe (content from 1–2% to 20–30%). The diversity of natural alloys based on Fe and Cu is a characteristic feature of the Volyn Lower Vendian basalts”.

Another important feature of the basaltic rocks is the high iron content and, simultaneously, the low sulfur content [4]. This indicates that the rocks contain little iron in the form of sulfides and sulfates. Predominantly, iron is present in the form of oxides, complex oxides, and hydroxides (see Table 5). In addition, the low sulfur content indicates that basaltic rocks contain little sulfide copper ore, which is the type most widely processed in industry [2].

Therefore, basaltic rocks with native copper mineralization should be classified as oxidized ores that contain primarily copper carbonates and silicates. The small amount of iron-sulfur minerals (Table 5) suggests that the use of pyrite flotation for basalts and associated rocks will be not very effective. Extraction of the Fe-Ti-V complex is possible by magnetic methods.

3.3 Investigation of magnetic separation of rocks. Basalt deposits contain native iron [5], as well as strongly magnetic magnetite and titanomagnetite (Table 5). Weakly magnetic minerals are virtually not extracted by magnetic separation at a typical field intensity of 0.16 T (separators of PBM, PBS type). During magnetic separation, native copper and copper minerals, being in the non-magnetic fraction, are very likely to concentrate in the magnetic separator tailing.

Experimental studies of dry magnetic separation were performed on individual size classes (-2.5 mm) of basalt, lava breccia, and tuff.

The aim was, first, to determine the quantity of the magnetic fraction, and second, to discover the possibility of concentrating copper in the separation tailings, which is relevant for developing a technology for copper extraction at the ore preparation stage.

Samples of the main copper-bearing rocks were taken from blasted rock mass at 10 sites of the Rafalivka basalt quarry. After averaging and crushing each sample in a crusher to -2.5 mm, they were subjected to dry magnetic separation under laboratory conditions using a drum magnetic separator PBSu-0.5/0.2. The averaged magnetic separation indicators are given in Tables 6–8.

Table 6 – Indicators of magnetic separation of basalt

Size class (mm)	Fraction yield, %	Cu content in feed %	Magnetic product, %			Non-magnetic product, %		
			yield	Cu content	Cu recovery	yield	Cu content	Cu recovery
-2.5+1.6	21.91	5.79	16.62	3.5	22.2	5.29	13.0	26.21
-1.6+0.8	27.46	3.33	21.91	0.37	3.1	5.54	15.0	31.68
-0.8+0.25	29.22	1.03	9.07	0.001	0.0	20.15	1.5	11.52
-0.25	21.41	0.65	7.56	0.0	0.0	13.85	1.0	5.28
Total	100.0	2.624	55.16	1.20	25.3	44.84	4.37	74.70

Table 7 – Indicators of the products of magnetic separation of lava breccia

Size class (mm)	Fraction yield, %	Cu content in feed %	Magnetic product, %			Non-magnetic product, %		
			yield	Cu content	Cu recovery	yield	Cu content	Cu recovery
-2.5+1.6	31.25	1.37	12.50	1.16	10.67	18.75	1.50	20.66
-1.6+0.25	52.81	0.89	20.63	0.24	3.65	32.19	1.30	30.8
-0.25	15.94	2.92	5.00	2.75	10.10	10.94	3.00	24.10
Total	100.0	1.36	38.13	0.87	24.42	61.88	1.66	75.58

Table 8 – Indicators of products of magnetic separation of tuff

Size class (mm)	Fraction yield, %	Cu content in feed %	Magnetic product, %			Non-magnetic product, %		
			yield	Cu content	Cu recovery	yield	Cu content	Cu recovery
–2.5+0.63	36.1	0.31	29.94	0.29	16.38	6.14	0.40	4.63
–0.63+0.1	22.7	0.45	19.09	0.42	15.13	3.65	0.60	4.13
–0.1	41.2	0.77	0.00	0.00	0.00	41.18	0.77	59.8
Total	100	0.53	49.03	0.34	31.5	50.97	0.71	68.6

For basalt (Tables 6), at a feed size of -2.5+0 mm to the separator, about 45% of the material reports to the non-magnetic fraction. The copper content in the tailings, compared to the initial feed, increases from 2.6% to 4.4%, i.e., there is a concentration of copper in the tailings by 1.7 times. At the same time, both products—magnetic and non-magnetic—have high copper contents that are above the cut-off grade (>0.35% Cu), so the separation tailings cannot be removed from the copper beneficiation process. This indicates insufficient liberation of the copper minerals in the feed and the necessity to reduce its particle size.

The experiments resulted in a high magnetic fraction yield of 55.16%. This is due to the coarse feed size, where many unliberated aggregates of magnetic minerals—both with copper and with waste rock—are attracted along with the liberated magnetic minerals. Because of this, the mass of concentrate is large, but most likely it is low in iron and requires grinding and re-separation. This is indicated by the experience of iron ore processing plants, where to liberate iron minerals, the ore is ground to 95% passing below 0.05 mm.

Table 6 for basalt shows, that the copper recovery in the non-magnetic product is 74.7%, which means a portion of the copper reports to the magnetic concentrate. The concentrate has an excessively high copper content of 1.2% and requires further treatment. This is also a consequence of insufficient liberation of the minerals.

Magnetic separation of basalt showed the possibility of concentrating copper in the tailings by 1.7 times. This indicator can be increased to 2–3 times by reducing the feed size. At the same time, finer grinding achieves an improvement in the iron grade of the magnetic product.

The separation indicators for lava breccia (Tables 7) overall are similar to those for basalt. The magnetic fraction yield is 38.13% versus 55.16% for basalt. Copper recovery to the magnetic concentrate is 24.42%, compared to 25.3% for basalt. Both the magnetic and non-magnetic fractions of the lava breccia have copper contents above the cut-off grade (0.87% and 1.66%, respectively). They require further treatment. The coarse feed size fractions contain a large number of intergrowths of copper and iron minerals, which cause copper to report to the magnetic product.

For tuff (Table 8), the highest copper recovery into the non-magnetic product is observed for the fine fractions. Particles of the coarse fractions (>0.25 mm) are divided approximately equally into the magnetic and non-magnetic products, while the finer fraction (-0.1 mm) goes almost entirely into the tailings. These fine fractions in the feed also have the highest copper content (0.77%), whereas in the magnetic concentrate of these fractions, copper is practically absent. Such behavior of grade and recovery is explained by the fact that in tuffs, copper is mainly finely disseminated.

The magnetic fraction yield during tuff separation is 50.97%. Some tuff samples had a sub-grade copper content (below 0.35%). These samples also showed a high magnetic product yield, averaging 54.6%, meaning the mass of tuff is reduced by about half, indicating a high content of iron minerals.

Copper recovery into the non-magnetic product is 68.6%, which is lower than for basalt (74.7%) and lava breccia (75.58%) at the same feed size. The degree of copper concentration in the tailings is low: in the feed 0.53% Cu, in the tailings 0.71% Cu. The tuff fractions reporting to the magnetic product contain iron and titanium. For example, the -2.5+0.63 mm fraction contains 36% Fe and 2.5% Ti; the -0.63+0.1 mm fraction contains 39% Fe and 4% Ti. Despite the lower copper content compared to basalts and lava breccias, tuff is a valuable raw material for obtaining by magnetic separation a concentrate that contains iron-titanium-vanadium.

It should be noted that increasing the number of cleaning stages on sequential separators, as proposed in [10], regardless of their field induction, does not improve the copper recovery into the non-magnetic product, because the amount of intergrowths in the initial feed of these operations is constant. The experience of iron ore and ilmenite processing plants indicates that for a given feed size, two separators – a primary and one cleaner – are sufficien.

To decrease the copper content in the magnetic product and increase the degree of copper concentration in the non-magnetic product, the feed size for magnetic separation should first be reduced. Then, based on the copper content in the magnetic and non-magnetic products, a decision can be made regarding their separate processing using copper flotation. At the same time, analysis of the magnetic product for titanium and vanadium content will demonstrate the need to extract these valuable metals, which is usually done by magnetic techniques.

4. Conclusions

It was established that the iron content is highest in tuffs (up to 18.2–21.6% Fe), in basalts up to 15.75%, in lava breccia up to 14.5%; the titanium content in tuffs is up to 2.63–2.18%, in basalts up to 2.4%, in lava breccia (in one quarry) more than 0.7%; the vanadium content is highest in lava breccia – up to 0.3% V, in tuffs up to 0.1%, in basalts up to 0.05%. In terms of vanadium pentoxide, the V_2O_5 content in lava breccia is up to 0.53%, in tuff 0.18%, in basalt 0.09%. These data meet industrial requirements; for example, titanomagnetite ores of the Kachkanar plant contain 14–

15% Fe and 0.12–0.14% V_2O_5, and are beneficiated by a traditional magnetic scheme.

A feature of the mineral composition of the basaltic rocks is the low quantity of sulfur-containing minerals, including sulfides and sulfates of copper and iron. The main magnetic minerals of the basaltic rocks are magnetite and titanomagnetite. When applying magnetic methods of beneficiation to these rocks, it should be kept in mind that in the structure of magnetite the iron ion is often replaced by titanium or vanadium. Mineralogical studies confirmed the presence in the basaltic rocks of natural alloys based on iron and copper with similar contents of these metals, as was first pointed out by Academician Lukin O.Yu.

Dry magnetic separation of the rocks was carried out at a feed size of –2.5 mm and a magnetic field induction of 0.16 T. The copper content in the initial feed was: for basalt 2.62%, for lava breccia 1.36%, for tuff 0.53%. The yield of the magnetic fraction and the possibility of concentrating copper in the non-magnetic product were investigated. It was found that the magnetic concentrate yield from basalt is 55.16%, from lava breccia 38.13%, from tuff 40.03%. Copper recovery into the magnetic separation tailings is: for basalt 74.7%, for lava breccia 75.58%, for tuff 68.6%. The use of magnetic separation is advisable at the ore preparation stage. Promising ways to increase copper recovery into the non-magnetic product are to reduce the feed particle size and to use wet magnetic separation instead of dry.

Conflict of interest

Authors state no conflict of interest.

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МЕТАЛОВМІСНА ФРАКЦІЯ ВОЛИНСЬКИХ БАЗАЛЬТІВ

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Анотація. Для базальтів Волинського Полісся і супутніх порід туфів та лавобрекчій дослідженнями геологів і вчених України були встановлені унікальні властивості щодо вмісту цінних металів, кольорових, чорних, благородних, рідкісноземельних. Практично значимим рудоутворюючим елементом визначена мідь, але поряд з нею, наприклад, залізо і срібло присутні в значній кількості і в самородній формі, тому часто базальтові родовища вважають поліметальними. Основна увага вчених приділялась міді, досліджувалося її розповсюдження на базальтових родовищах і способи вилучення. Проблемою технологій переробки, що розробляються, є відокремлення металів один від одного. Очевидно, що на завершальному циклі переробки, це виконується пірометалургійними і гідрометалургійними способами, але на стадії рудопідготовки можливе використання фізичних способів електричної і магнітної сепарації. Розвиток фізичних процесів переробки базальтової сировини наразі продовжується. В цьому плані метою статті є аналіз залізовмісної фракції в базальтових породах, що наразі досліджено недостатньо. Для аналізу застосовані методи спектроскопічного, мінералогічного аналізу, сухої магнітної сепарації окремих класів крупності порід. Встановлено, що залізовмісна фракція представлена переважно залізом, титаном, ванадієм, їх кількість в кілька разів вище фонових значень. Вміст металів становить: в базальті до 15,75% Fe, 2,4% Ti, 0,05% V або 0,09% V_2O_5; в лавобрекчії до 14,5% Fe, більше 0,7% Ti, 0,3% V, або 0,53% V_2O_5; в туфі до 18,2–21,6% Fe, 2,63–2,18% Ti, 0,1% V або 0,18% V_2O_5. Особливостями мінералогічного складу порід є мала кількість сульфідів та сульфатів міді і заліза, наявність природних сплавів міді і заліза. Магнітна складова представлена магнетитом і титаномагнетитом. Дослідження сухої магнітної сепарації порід виконане для крупності живлення 2,5 + 0 мм при індукції магнітного поля 0,16 Тл. Вміст міді у вихідному живленні становив: для базальту 2,62%, лавобрекчії 1,36 %, туфу 0,53%. Досліджувався вихід магнітної фракції і можливість концентрації міді в немагнітному продукті. Встановлено, що вихід магнітного концентрату з базальту становить 55,16% від вихідної проби, концентрату з лавобрекчії 38,13%, з туфу 40,03%. Вилучення міді у відходи магнітної сепарації становить: для базальту 74,7%, для лавобрекчії 75,58 %, для туфу 68,6%. Використання магнітної сепарації доцільне на стадії рудопідготовки. Перспективними напрямками підвищення вилучення міді в немагнітний продукт є зменшення крупності живлення і застосування мокрої магнітної сепарації замість сухої.

Ключові слова: базальт, туф, лавабрекчія, магнітна сепарація.