

SHORT
COMMUNICATIONS

On the Quantitative Evaluation of the Neutralizing Potential of Host Rocks

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When sulfide ores are mined and processed and dump rocks and tailings are stored, one of the most important problems is the formation of acid drainage waters, which are produced during the oxidation of residual sulfides by atmospheric precipitates [1–4]. The potential possibility of this process, which is usually referred to in the modern literature as acid mine drainage, is predetermined mostly by the composition and proportions of sulfides and gangue minerals that react with “water” in various geochemical environments [5, 6]. Our research was aimed at developing methodological approaches for the evaluation of the acid–base potential of rocks (i.e., the balance between their ability to produce and neutralize acids) on the basis of experimentally obtained data. This approach was developed using the 154 samples of host rocks from the Veduga gold deposit in the Yenisei Kryazh Range. The deposit is now prepared for active mining. The Veduga deposit is characterized by generally low contents of sulfides, which include pyrite, arsenopyrite, and pyrrhotite and whose amounts commonly do not exceed 5–7%. The orebodies are hosted by metasomatic rocks (sericitolites) cut by quartz and carbonate–quartz veinlets and include lenses of these minerals and disseminated sulfide mineralization [7].

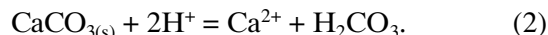
The evaluation of the potential of the rocks involved the following operations.

(1) The neutralizing potential (NP) of the rocks was determined in the process of reaction between 2 g of a rock sample (<0.25 mm) with an standard HCl solution (0.1 or 0.5 N) with the subsequent back titration of the remaining acid to pH 7 with an NaOH solution of analogous normality. In order to determine the normality of the acid and alkali needed for the test, we preliminarily determined how intensely the sample hissed when reacting with HCl diluted to 1 : 3. The conventional method [8] was modernized by utilizing the bromine-cresol red indicator for the more accurate identification of the color transition from acid to neutral pH values. Within the scope of the assumptions [8], the neutralizing potential of rocks corresponds to a value expressed

through the tonnage of CaCO₃ equivalent per thousand tons of the rock (i.e., ppt = 0.1 wt %). Based on experimental data, this potential is calculated as:

$$\Sigma NP = HCl_{\text{cons}} \times 25 \times N_{\text{HCl}}, \quad (1)$$

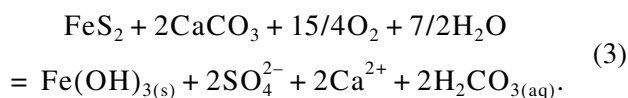
where HCl_{cons} is the amount of HCl consumed in the reaction with the rock sample; N_{HCl} is the normality of the acid; and the coefficient of 25 is the equivalent factor, which is calculated from the molar and weight proportions of the reaction:



One mol of HCl is neutralized by 0.5 g-mol of calcite. If the neutralization of a 2-g sample consumes x mol of acid (HCl_{cons}), this requires $1/2 x$ g-mol of CaCO_{3(s)}. The reaction with a 1000-g (1-kg) sample should require $250x$ g-mol of CaCO_{3(s)}, whose molecular weight was rounded to 100 g. Finally, $25x$ t of CaCO_{3(s)} will react to neutralize the acid that can be released by 1000 t of this rock.

(2) The amount of CO₂ (wt %) was determined in the samples by titrimetric methods and recalculated to CaCO_{3(s)} (wt %). Inasmuch as acid can be consumed in (1) to the dissolution of various minerals, this procedure makes it possible to quantify the contribution of carbonates alone.

(3) The total and sulfate sulfur concentrations were determined by the weight method, and the concentration of sulfide sulfur was calculated as the difference between them. Based on analytical data on the contents of sulfide sulfur in the samples, we calculated the acid-producing potential (AP) by method [9] with S_{total} substituted for S_{sulfide}. We believe that this leads to more accurate AP values, particularly if the rock is rich in sulfates like gypsum or barite:



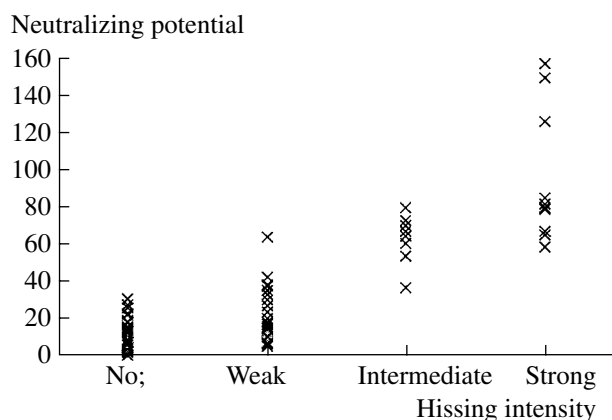


Fig. 1. Neutralizing potential values of the rocks depending on the hissing intensity of the samples when reacting with HCl diluted to 1 : 3.

The stoichiometry of reaction (3) indicates that the neutralization of sulfuric acid released during the oxidation of 1 g-mol of pyrite requires 2 g-mol of calcite, which implies that each gram of sulfur requires 3.125 g of $\text{CaCO}_3(\text{s})$. For the convenience of comparison, NP and AP should be expressed in the same units, for example, ppt, as was recommended in [8, 9]. The multiplication of the obtained wt % by 10 leads to the formula

$$\text{AP} = S_{\text{sulfide}} (\text{wt } \%) \times 31.25. \quad (4)$$

In fact, we determined the amount of the CaCO_3 equivalent in the rock in the former case and the amount of sulfuric acid required for neutralization in the latter case. Knowing these values, one can calculate the resulting potential as the difference $\Sigma\text{NP} - \text{AP}$.

(4) We instrumentally determined the pH of the aqueous leachates (R/W = 1 : 4) using an ESK-10601/7 combined glass electrode on an EKSPERT-001 device. The value thus obtained enabled us to compare the calculated ($\Sigma\text{NP} - \text{AP}$) and measured values of the result-

ant potentials, of course, with regard for the duration of the experiments (24 h) modeling water-rock interactions.

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Figure 1 shows the relations between the qualitative (visual assessment of the intensity of the during the reaction with HCl) and quantitative (ΣNP) characteristics of our rock samples. Their obvious correlation demonstrates the usefulness of the quantitative test, which can be *in-situ* applied to a great number of samples. The Veduga deposit host rocks, the examination of 95 samples from it indicate that these rocks have low ΣNP . For example, 76 of these samples have $\text{NP} < 50$ ppt (5 wt % CaCO_3 -equiv.) and only 19 of them are characterized by higher NP with the maximum values of $\text{NP} > 80$ ppt determined only in five of them.

Figure 2 displays the symbiotic variations in the calculated ΣNP values and the $\text{CaCO}_3(\text{sol})$ concentration in the samples. The total potential of the rocks is generally higher than that accounted for by carbonates alone ($\text{NP}_{\text{car}} = \text{CaCO}_3, \text{ wt } \%$), although their correlation is obvious and is particularly clear for samples with high NP, such as samples 188, 198, 255, 256, and 283. This led us to propose that these rocks can be utilized as geochemical barriers, for example, around the tailing heaps that will be created during ore processing and that are usually richer in sulfides [3].

In Fig. 3, the values of the resultant neutralizing potential of our selection of rock samples are compared with the acid-producing potential. This figure also shows the line of their equal values (in ppt) [5]. The NP values of our rock samples are mostly lower than 50 ppt. Nevertheless, the rocks whose data points lie below this line can, theoretically, produce solutions with low pH when interacting with water, as was tested

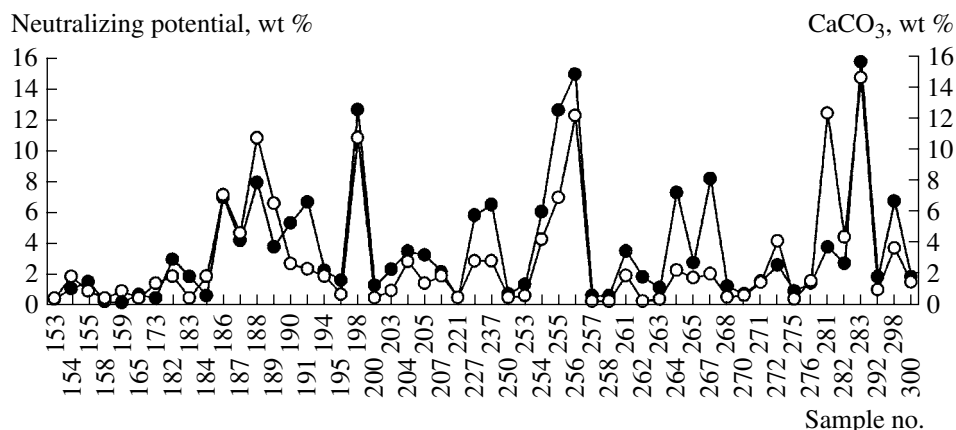


Fig. 2. Dependence of the total neutralizing potential (solid circles, scale on the left-hand side) and $\text{CaCO}_3(\text{s})$ content in samples of dumped rocks from the Veduga deposit (open circles, scale on the right-hand side).

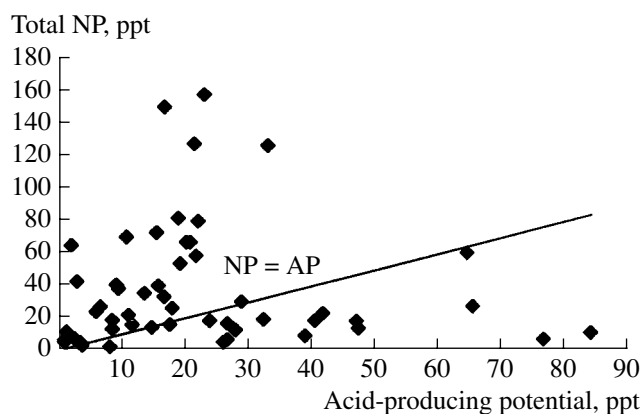


Fig. 3. Calculated values of the neutralizing and acid-producing potentials (the line shows their equal values).

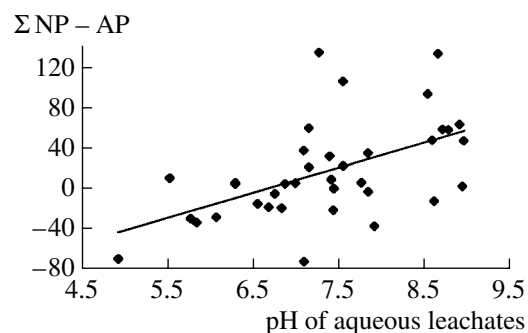


Fig. 4. Resultant potential ($\Sigma NP - AP$) of the rock samples and the pH of their aqueous leachates. The linear correlation coefficient $R^2 = 0.29$.

using their aqueous leachates. An undoubtedly favorable factor is the fact that only four of our samples have significant AP thanks to the generally low sulfide contents.

The final value is the resultant potential, which is equal to the ($\Sigma NP - AP$) difference. Figure 4 shows the values of ($\Sigma NP - AP$) for our rock samples and the pH of aqueous leachates from them. In spite of the low approximation coefficient ($R^2 = 0.29$), a positive correlation of these values is quite clear. This correlation is pronounced even more clearly in Fig. 5, in which the selections of rock samples are characterized not only by their resultant potential and pH but also by their deviation from zero and from the neutral points of the solutions. The meaning of the comparison is that rocks with negative values of the ($\Sigma NP - AP$) values should yield less acidic ($pH < 7$) aqueous leachates in rock-water reactions and vice versa. This principle is best of all applicable to samples 253, 270, 275, and 292,

whereas, for example, sample 263 has one of the lowest ($\Sigma NP - AP$) values and pH 7.1 of its aqueous leachate. The aforementioned four samples with a high acid-producing potential were leached by water for 20 weeks in flow-through reactors [10]. Not touching here upon the behavior of heavy metals and anions, we would only like to mention that the pH decreased even more significantly in these kinetic tests: 253 (5.83/3.70), 270 (4.92/3.48), 275 (5.76/4.12), and 292 (6.06/4.24), where the numerators in parentheses correspond to the pH of the aqueous leachates and the denominators show the pH of the leaching solutions. This validates our conclusions.

Considered together, the results of our chemical, analytical, and experimental studies offer the possibility of the reliable evaluation of the geochemical characteristics of the rocks hosting the Veduga deposit. Our results indicate that these rocks possess a sufficient potential for neutralizing the sulfuric acid produced by the oxidation of residual sulfides. Moreover, it should

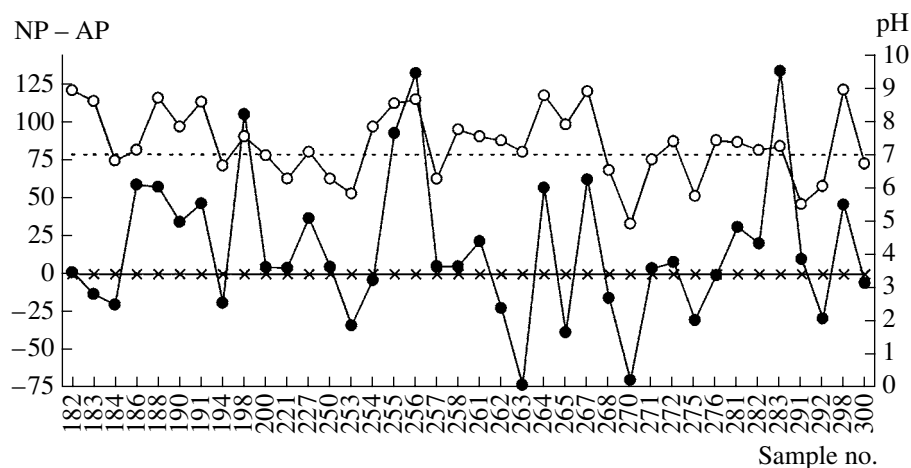


Fig. 5. Resultant potential of dumped rocks equal to the difference between the ($\Sigma NP - AP$) values (solid circles, scale on the left-hand side) and the pH of the aqueous leachates (open circles, scale on the right-hand side). The straight line with crosses corresponds to equal NP and AP values, and the dashed line shows neutral pH values (normal conditions).

be taken into account that we analyzed rocks of various types, which were carefully selected in the process of sampling according to their morphology and composition. Of course, the acid–basic characteristics of the dumped rocks will be somewhat equalized, as also will be their potentials. Nevertheless, careful preliminary quantitative studies and assessment of newly developed industrial sites are advisable in order to minimize the possible harmful environmental impact. This led us to recommend the methods described above for the examination of other ore fields. The methodological approach can be recommended as the basis for the systematics of sulfide-bearing wall and stripping rocks of various geochemical types.

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