

Effect of Particle Size on Solubility and Neutralizing Ability of Carbonate Minerals

VICTOR N. MAKAROV, OLGA P. KORYTNAYA, ALLA S. LUGOVSKAYA, TATIANA N. VASILIEVA
and DMITRIY V. MAKAROV

*Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Sources,
Kola Scientific Centre of the Russian Academy of Sciences,
Ul. Fersmana 26a, Apatity 184200 (Russia)*

E-mail: makarovdv@chemy.kalasc.net.ru

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Abstract

The effect of particle size of carbonate minerals (dolomite and calcite) on the kinetics of their interaction with water and ferrous sulphate solution is investigated. It is established that the efficiency of solution neutralization is to a noticeable extent determined by the particle size of the reagent. The application of calcite as a material for the construction of artificial geochemical barriers is preferential over dolomite. In the case when reagent consumption is much higher than the stoichiometric amount, or under lengthy interaction (for example, in filtering dams of artificial geochemical barriers) the particle size of the material has no substantial effect.

INTRODUCTION

Attention of home and foreign researchers to sulphide-containing wastes of mining and smelting plants is explained by the fact that these wastes cause a substantial increase in the load on the environment due to a decrease in the level of pH of underground and surface waters (acid rock drainage) and an increase in the concentration of heavy metals in them [1, *etc.*]. At the same time, these wastes are sometimes considered as technogenic deposits [2–4].

Nonmetallic minerals present in the mining and smelting wastes sometimes act as geochemical barriers and cause a substantial decrease in the concentrations of heavy metals entering the environment [5, 6]. The major part of nonmetallic minerals is more stable to the action of supergene processes than sulphides are. However, the level of nonmetallic minerals in mining and smelting wastes is 1–2 orders of magnitude higher than that of sulphides. Because of this, the effect of changes in their status both on the environment and on tech-

nological properties of technogenic deposits can be very essential. The most important barrier is the change in pH of the medium at the boundary between the ore minerals under oxidation or the resulting sulphates and nonmetallic minerals which are unstable toward weathering. The latter include carbonates, chlorites, serpentine minerals, micas [7, 8].

In the cases when sulphide content is comparable with the content of nonmetallic minerals and the latter are stable to weathering, it is reasonable to make artificial geochemical barriers using various rocks.

Carbonate minerals are the most promising material for artificial geochemical barriers preventing acid wastes containing heavy metals from penetrating into the environment from mining and smelting waste storages and from technogenic deposits. Such a barrier should possess high efficiency, that is, it should actively react with acidic solutions, but at the same time it should be characterized by high filtering ability. The latter is especially urgent in connection with the fact that the volume of

the solid phase newly formed in neutralization of an acid, firstly of acidic salts, can exceed the volume of the initial solid phases. Therefore, the volume of space between grains will decrease with time, which will cause a decrease in filtration coefficient and rate. Because of this, the application of a material with larger particle size would allow a longer period of time before its replacement. On the other hand, an increase in particle size causes a decrease in the specific surface of a reagent. Since dissolution and neutralization occur on the surface of the solid and liquid phases, a decrease in specific surface would cause a decrease in the process rate. In order to choose an optimal version, it is necessary in every specific case to examine the dependence of rates of dissolution and neutralization of the acid salts on the particle size of carbonates.

EXPERIMENTAL

Calcite and dolomite of the following particle size classes were used, mm: $-1.0 + 0.4$, $-0.2 + 0.1$, $-0.1 + 0.073$, $-0.073 + 0.05$, $-0.05 + 0.025$ and $-0.025 + 0$. In order to estimate dissolution rate, distilled water was used; a solution of 0.025 M FeSO_4 was used to estimate the rate of neutralization of the acidic salt. This concentration was chosen taking into account the solubility of gypsum formed by neutralization of ferrous sulphate: the concentration of gypsum should be below saturation in order to avoid passivation of the carbonate surface by the resulting sulphate. The consumption of carbonate was 5 g/l in the first case; in the second, it was 5 and 10 g/l.

RESULTS AND DISCUSSION

The particle size of calcite has a noticeable effect on pH during the dissolution of the mineral in distilled water within the first period of time, lasting for 10–20 min. The fine material with the smallest particle size (below 0.1 mm) provides pH from 9.4 to 9.85 (Fig. 1), and the maximal value is established either almost instantly (for particle size less than 0.05 mm) or within the first 10 minutes. Carbonate with larger particles gets dissolved more

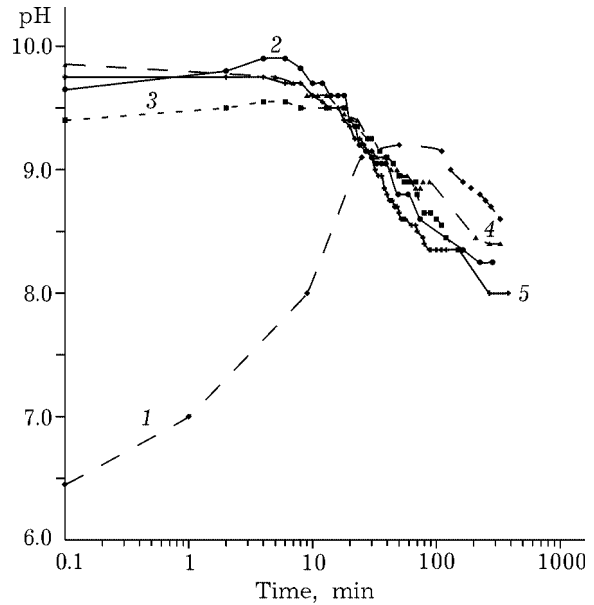
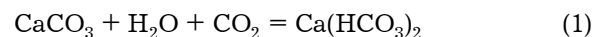


Fig. 1. Dependence of pH of distilled water on the time of interaction with calcium carbonate for its consumption equal to 5 g/l. Particle size, mm: $-1.0 + 0.4$ (1), $-0.1 + 0.073$ (2), $-0.073 + 0.05$ (3), $-0.05 + 0.025$ (4), $-0.025 + 0$ (5).

slowly. Maximal pH value is achieved after 25–30 min. Then, independently of particle size, pH of the solution starts to decrease; its final value gets established after 250–350 min at the level of 8–8.5.

Such a behaviour of pH changes with time is due to the consumption of the dissolved carbon dioxide, which accompanies the initial period of calcite dissolution:



Local equilibrium is established between calcite and solution; however, no equilibrium is achieved at that moment between the solution and the atmosphere. This corresponds to the maximal pH of solution. As the lack of carbon dioxide in solution is compensated by the atmosphere, the acidity of solution increases and reaches a stable level after the complete equilibrium between the solid phase, solution and atmosphere is achieved.

A more complicated behaviour is observed for the neutralization of iron sulphate by calcite (Fig. 2, a). In technogenic sulphate-containing units, the formation of ferrous sulphate occurs during the oxidation of sulphide minerals, mainly pyrite, marcasite and pyrrhotite [1]. For pyrite, the reaction looks like follows:

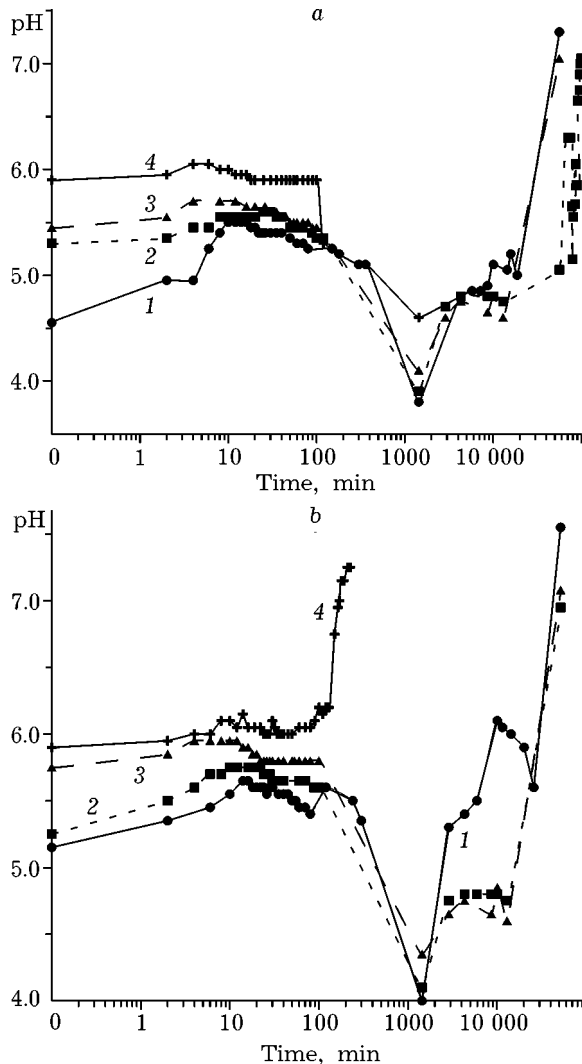
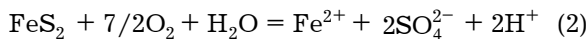
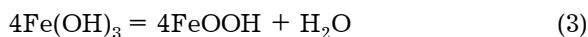
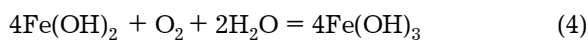
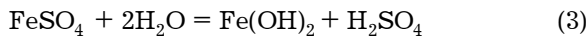


Fig. 2. Dependence of pH of FeSO_4 solution (0.025 M) on the time of interaction with calcium carbonate for its consumption: 5 (a) and 10 g/l (b). Particle size, mm: $-0.1 + 0.073$ (1), $-0.073 + 0.05$ (2), $-0.05 + 0.025$ (3), $-0.025 + 0$ (4).



As a result of sulphate hydrolysis, iron (II) hydroxide is formed, which later is oxidized to iron (III) hydroxide:



The transfer through the film of precipitated hydroxides during the neutralization of acid salt solutions can be represented by several stages:

- Transport of H^+ ions from the solution volume to the boundary liquid film surrounding the hydroxide layer;

- Diffusion of H^+ ions through the boundary layer;
- Transfer of H^+ ions through the interface into the hydrated hydroxide layer;
- Diffusion of H^+ ions through the hydrated hydroxide layer to the surface of carbonate grain;
- Transfer of H^+ ions through the interface: hydrated hydroxide layer - carbonate grain;
- Chemical reaction



- Diffusion of Ca^{2+} and ions through the interface: carbonate grain - hydrated hydroxide layer;
- Diffusion of Ca^{2+} and ions through the hydrated hydroxide layer;
- Transition of Ca^{2+} and ions through the interface from the hydrated hydroxide layer into the boundary layer;
- Diffusion of Ca^{2+} and ions through the diffusion layer;
- Diffusion of Ca^{2+} and ions into the solution.

Total rate of the process is limited by the diffusion of ions through the hydrated hydroxide layer.

With the stoichiometric consumption of carbonate 5 g/l, similarly to the first case, pH of the solution substantially depends on the particle size of the material within the initial period (10–80 min). For the material with particle size $-0.1 + 0.073$ mm, pH is established as early as after 10–15 s at the level of 4.55; for $-0.073 + 0.05$ mm, it is 5.3; for $-0.05 + 0.025$, 5.45; for $-0.025 + 0$ mm, 5.9. With an increase in interaction time to 70–80 min, a small increase in pH is observed only for the carbonate with the largest particle size ($-0.1 + 0.073$ mm). In other experiments, pH was only slightly changed during this period. Further on, a sharp decrease in pH was observed in all the experiments. Here, the differences in particle size did not play any substantial part. After 1440 min, pH reaches its minimal value: from 3.8 for the $-0.1 + 0.073$ mm particle size class to 4.6 for the $-0.025 + 0$ mm class. After that, a slow increase in pH is observed, and after 56 000–99 000 min (36–69 days) the solution passes into the alkaline region.

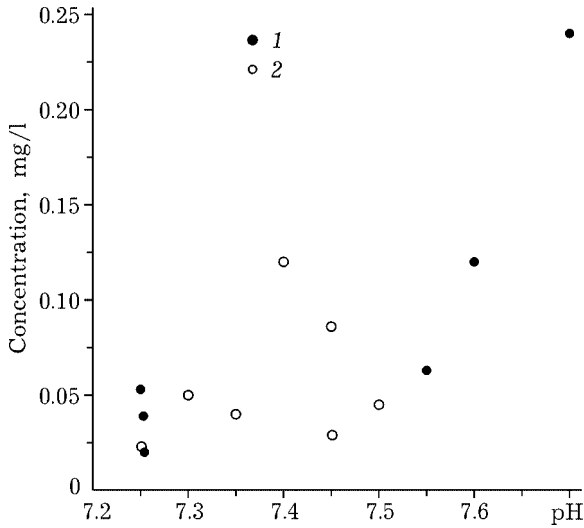


Fig. 3. Residual concentration of ferrous ions in solution in experiments with calcite (1) and dolomite (2).

A 2-fold increase in the consumption of carbonate of the three larger classes did not bring about any principal changes into the character of pH dependence on time of interaction in the 0.025 M FeSO₄ solution and on particle size of calcium carbonate (see Fig. 2, b). However, for the carbonate with the smallest particle size (-0.025 + 0 mm) the dependence is substantially different from the former one. For 120 min, pH

of solution remains almost constant (5.9-6.2), but then increases rapidly to 6.95-7.25. The residual iron concentration in solution did not exceed 0.25 mg/l in all cases and was independent of either reagent consumption or its particle size; nor of the final pH (Fig. 3).

Since dolomite dissolves much slower than calcite, substantial differences in pH of solution are observed in the initial period in the case of equal particle size of both reagents (Fig. 4). In the case of dolomite, pH is much lower than for calcite. With an increase in the particle size of reagents, the difference increases. With dolomite, the dependence of pH on particle size within the initial 50-80 min is exhibited more vividly (Fig. 5); however, these differences decrease with time.

For the dissolution of calcite with large particle size, a clearly exhibited maximum of pH is observed (see Fig. 1); for the dissolution of coarse fractions of dolomite, we observe a smooth increase in pH till its complete stabilization. However, for the dissolution of small fractions, pH rapidly increases during the initial period, but then decreases gradually (see Fig. 5). Maximum values of pH are achieved after 4-10 min.

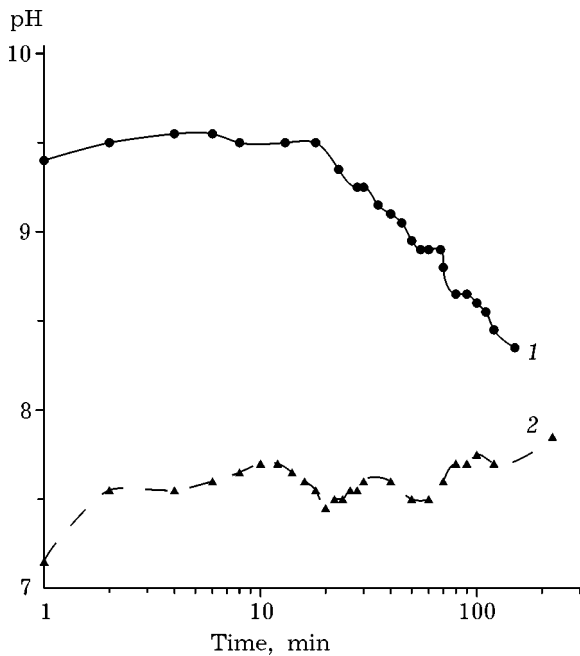


Fig. 4. Dependence of pH of distilled water on the time of interaction with calcium carbonate (1) and dolomite (2) of equal particle size (-0.1 + 0.073 mm) for 5 g/l consumption of both reagents.

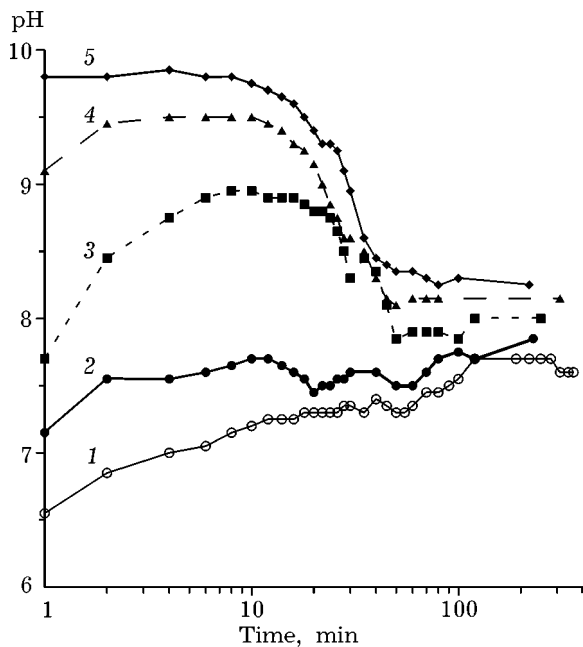


Fig. 5. Dependence of pH of distilled water on the time of interaction with dolomite for its consumption equal to 5 g/l. Particle size, mm: -1.0 + 0.4 (1), -0.1 + 0.073 (2), -0.073 + 0.05 (3), -0.05 + 0.025 (4), -0.025 + 0 (5).

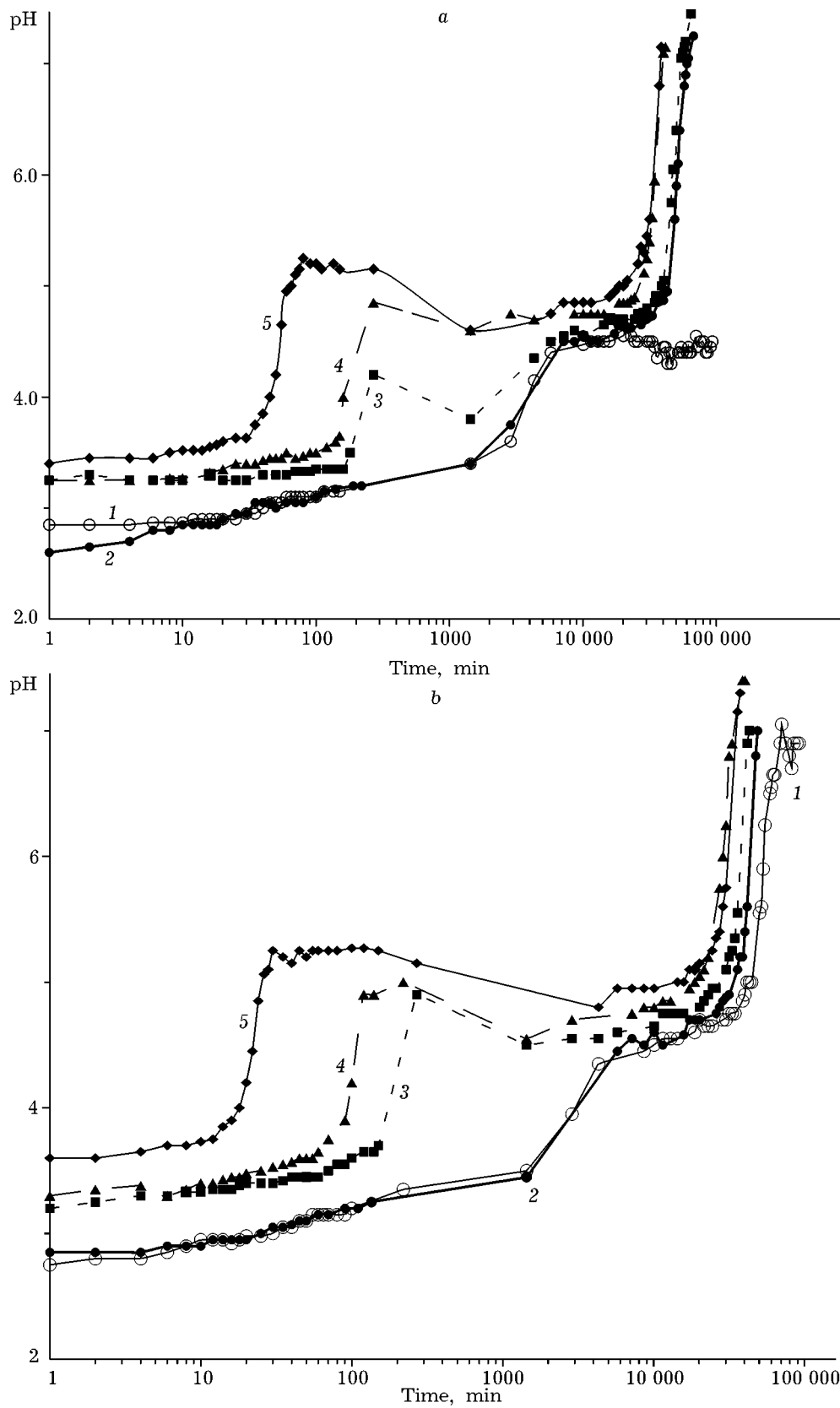


Fig. 6. Dependence of pH of FeSO₄ solution (0.025 M) on the time of interaction with dolomite for its consumption equal to 5 g/l. Particle size, mm: -1.0 + 0.4 (1), -0.1 + 0.073 (2), -0.073 + 0.05 (3), -0.05 + 0.025 (4), -0.025 + 0 (5).

The interaction of dolomite with ferrous sulphate proceeds much slower than that in the case of calcite (Fig. 6, *a*). Within the first 45 min, independently of particle size, pH of solution does not exceed 4. After 1.5 h, when the smallest fraction is used (smaller than 0.025 mm), pH increases to 5.25, then again decreases. For larger fractions ($-0.073 + 0.05$ and $0.05 + 0.025$ mm), a less clearly exhibited local maximum is established somewhat later: after 270 min. For coarse fractions, a very weakly exhibited maximum is observed only after 15 days.

With the smallest dolomite particles (smaller than 0.025 mm), the alkaline medium is established in about a month; for the material with particle size $-0.05 + 0.025$ mm, in a month and a half; for larger fractions ($-0.073 + 0.05$ and $-0.1 + 0.073$ mm), in 1.5–2 months. With the largest fraction, the alkaline medium is not established in solution even in 2–2.5 months.

A 2-fold increase in the reagent consumption does not cause any principal changes in the character of the process during the initial period. However, by the end of experiment, after treatment for 2 months, even with the largest fraction, pH of solution approaches 7 (see Fig. 6, *b*).

CONCLUSIONS

1. The application of calcite as a material for artificial geochemical barriers is preferable.

2. The application of dolomite is inexpedient for neutralization of the solutions of acid salts in surface water reservoirs when interaction time is limited by the rate of reagent sedimentation on the bottom.

3. The reagent particle size affects the efficiency of neutralization of solution. However, in case when the consumption of reagent is substantially higher than the stoichiometric one, or for a long interaction time (for example, in filtering dams of artificial geochemical barriers) the material particle size does not play any substantial role.

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