MODIFICATION OF MAGNETIC PROPERTIES OF SIDERITE BY RADIATION PRETREATMENT WITH ACCELERATED ELECTRONS

Theoretical knowledge of ionization radiation of accelerated electrons was used as a basis for investigation of conditions of its use in modification of magnetic properties of siderite. Experiments confirmed the positive effect of irradiation with accelerated electrons on magnetic susceptibility of siderite, which showed a 20-fold increase. This change resulted from thrmic decomposition of siderite and formation of new ferromagnetic phases on its surface. The magnitude of radiation dose and oxidation conditions of siderite are the decisive factors in this process.

1. INTRODUCTION

Modification of magnetic properties of useful minerals extends the possibilities of their processing by technologically and economically advantageous methods of magnetic separation. In the case of weak-magnetic minerals, which also include siderite, the approach mentioned improves their magnetic susceptibility to such a degree that economically most advantageous method of separation in a weak magnetic field can be used for their treatment. The process of modification of magnetic properties of minerals can be realized in several ways, the radiation pretreatment with accelerated electrons being one of the latest.

Minerals irradiated with accelerated electrons accumulate kinetic energy which is changed to heat. From the microstructural viewpoint, this process can be described as interactions of accelerated electrons with microparticles of the irradiated mineral which occur in the form of elastic and inelastic collisions or bremsstrahlung radiation.

Inelastic electron collisions lead to excitation of electrons of the irradiated mineral from their basic states to higher energetical levels or even pulling them out of the electron envelope, using in this way a considerable part of their energy. More frequent elastic collisions are manifested only by deflection of paths of accelerated electrons from the original direction of movement. Bremsstrahlung radiation is an outcome of deceleration of the motion of an accelerated electron as it passes close to an atom nucleus. While the energy of an inelastic collision of electrons changes to heat only gradually during the return of electrons to their original energetic levels, in case of elastic collisions and bremsstrahlung an immediate production of heat is observed. Practically all the energy of accelerated electrons adsorbed in the irradiated mineral is thus converted to heat. The only exception is the energy expended on possible changes of chemical bonds. Developed heat causes thrmic decomposition of minerals leading to formation of new phases on their surfaces which frequently display better magnetic properties (Broz, 1975).

Radiation pretreatment of minerals with accelerated electrons for the purpose of modification of their magnetic properties has been verified experimentally mainly on chalcopyrite (Florek and Cerny, 1992) and indirectly technologically on siderite (Rostovc et al. 1989) as well. This work summarizes additional information on conditions and results of siderite irradiation.

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2. THEORETICAL PART

Modification of magnetic properties of siderite by means of irradiation with accelerated electrons presupposes such temperature which gives rise to its thermic decomposition and the development of a phase having higher magnetic susceptibility. These conditions are fulfilled in the temperature range 400-600 °C in which the oxidation of siderite occurs at the access of air, according to chemical formulas

\[ 6 \text{FeCO}_3 + \text{O}_2 = 2 \text{Fe}_3\text{O}_4 + 6 \text{CO}_2 \]  \hspace{1cm} (1)

\[ 4 \text{FeCO}_3 + \text{O}_2 = 2 \text{Fe}_2\text{O}_3 + 4 \text{CO}_2 \]  \hspace{1cm} (2)

The mixture of maghemite, hematite and magnetite forms the product of oxidation of siderite under the above conditions. Lower temperatures give rise to Fe$_3$O$_4$ in the form of ferromagnetic maghemite (γ-Fe$_2$O$_3$). Increased temperatures and lengthened times of oxidation change cubic maghemite to hexagonal paramagnetic hematite (α-Fe$_2$O$_3$). (Broz, 1975). In order to modify magnetic properties of siderite it is, therefore, advantageous to heat it up quickly in the air up to 600 °C to obtain ferromagnetic products, magnetite according to formula (1) or maghemite according to formula (2). Reaching of these temperatures depends on the dose of accelerated electrons.

The following relationship may be used to determine the dose of accelerated electrons in Gy units

\[ D = C \cdot \Delta T \]  \hspace{1cm} (3)

where \( D \) is the energy dose of accelerated electrons [kJ·kg⁻¹],

\( C \) - specific heat of irradiated mineral [kJ·kg⁻¹·K⁻¹],

\( \Delta T \) - the temperature increase of the mineral due to irradiation [°K].

In the case of siderite, with specific heat 807.57 J·kg⁻¹·K⁻¹, the doses 306.88 Gy or 468.39 Gy are required according to (3) to attain the temperature increase to 400 °C or 600 °C, respectively. On the assumption that energy losses of electrons caused by their rebound, secondary emission of electrons, induced X-ray radiation or radiation of produced heat, do not exceed values provided in literature on the use of electron furnaces, the coefficient of energy utilization equal to 0.5 can be considered in the case of irradiation of siderite with accelerated electrons. If this is the case, the calculated energy doses of accelerated electrons should be doubled.

3. EXPERIMENTAL PART

Experiments with modification of magnetic properties by irradiation with accelerated electrons were conducted using siderite from the Rudnany deposit in East Slovakia, containing 43.57% Fe, of which Fe$^{2+}$ amounted to only 0.46%. The grain size of its specimens corresponded to standard classes in the interval below 6 mm.

Samples were irradiated with accelerated electrons in a linear accelerator of the LINAC 4-1200 type, made by Tesla - Vakuova Technika, s.€. Prague. The energy range of accelerated electrons produced by this accelerator was 3,5-5 MeV, the medium current of the fast electron beam amounted to 300 μA, the medium output was up to 1,2 kW and the pulse duration 2,7 μs. The current intensity of the fast beam and the time of use were to regulated to the dose of accelerated
electrons during irradiation. Siderite was irradiated in the air in an open aluminium case and cooled to the room temperature under identical conditions.

An automatic apparatus Kappabridge KLY-2, manufactured by Geofyzika, s.e. Brno, was used to measure magnetic properties of siderite. This apparatus allows to determine volumetric and specific magnetic susceptibilities of granular paramagnetic materials in the range from $10^{-4}$ to 0.2 of SI units at a sensitivity $4 \times 10^4$ SI of units.

The method of X-ray diffraction powder analysis employing the apparatus DRON 2.0, as well as chemical quantitative analyses were used to investigate the phase changes of irradiated samples of siderite.

4. DISCUSSION

Results of experiments on irradiation of siderite with accelerated electrons, presented partially in Table 1, confirmed the essential importance of the thermal effect, and of thermic decomposition resulting from this effect, on modification of magnetic properties of this mineral. Siderite irradiated with a high energy dose of accelerated electrons of 400 kGy, emitted during 10 min at a low intensity of electron current in such a way that its temperature did not increase, showed no changes of magnetic susceptibility. Such changes occurred only at intensive irradiation of siderite with an identical dose which produced a thermic effect on its surface. This procedure, using current intensity of accelerated electrons 5.4 $\mu$A cm$^{-2}$ and increasing time of irradiation in the interval 80-140 s, was used to investigate the relationship between the magnetic susceptibility and the radiation dose (Table 1).

Table 1. Influence of irradiation with accelerated electrons on magnetic susceptibility of siderite

<table>
<thead>
<tr>
<th>Radiation dose $10^3$ Gy [J·kg$^{-1}$]</th>
<th>Volumetric magnetic susceptibility [10$^{-6}$ SI units] before and after irradiation</th>
<th>Index of growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>1.135 before and 1.307 after irradiation</td>
<td>1.15</td>
</tr>
<tr>
<td>1200</td>
<td>1.132 before and 1.624 after irradiation</td>
<td>1.43</td>
</tr>
<tr>
<td>1500</td>
<td>1.133 before and 1.883 after irradiation</td>
<td>1.66</td>
</tr>
<tr>
<td>1800</td>
<td>1.140 before and 3.316 after irradiation</td>
<td>2.90</td>
</tr>
<tr>
<td>2400</td>
<td>1.136 before and 2.1822 after irradiation</td>
<td>19.20</td>
</tr>
</tbody>
</table>

The exponential character of this relationship confirms the possibility of a significant increase of magnetic susceptibility, reaching values as high as 20-fold of the original value at a dose 2 400 kGy. The doses of accelerated electrons which provoked changes of magnetic susceptibility of siderite were 4-fold higher than their calculated values. This can be explained by the fact that the calculation did not take into account the important factors affecting the irradiation effect, such as penetration of radiation into a mineral and directional characteristics of the source. However, it is difficult to assess the effect of these factors, therefore the results of experiments can be used for the moment to determine the radiation dose with the highest possible accuracy.

X-ray diffraction analysis was used to evaluate the degree of thermic decomposition of irradiated siderite samples. Diffraction patterns of the original and irradiated samples of siderite, illustrated in Fig. 1, confirmed the presence of new phases after the irradiation. Diffraction lines
identified not only siderite but also calcite and potassium aluminosilicate hydroxide - illite. The irradiated sample shows a decrease of the intensity of diffracted radiation in lines corresponding to siderite which suggests the decrease of its quantity (Fig. 1b). Simultaneously detected new diffraction lines indicate the presence of magnetite and maghemite, distinguishing of which poses some problems due to very close values of their interplanar spacing. The development of these phases confirms the fact that irradiation of siderite produces temperatures needed for its oxidation according to the relation (2). The absence of hematite, which develops when the temperature and time of thermic decomposition of siderite increases, suggests the high rate of irradiation process and subsequent oxidation. A course such as this is highly desirable from the viewpoint of magnetic properties of siderite because it gives rise to a maximal number of ferromagnetic phases.

The process of oxidation at irradiation of siderite with accelerated electrons takes place only on the surface of this mineral. The thickness of the newly developed ferromagnetic phase depends on the temperature produced by irradiation and on good access of air to individual siderite grains.
The calculation, confirmed by the experiment, showed that magnetic susceptibility of a siderite grain of spherical shape, 1 mm in diameter, increased by the factor of 20 when a ferromagnetic layer of maghemite and magnetite, 8·10³ mm thick, developed on its surface. Localization of the magnetic susceptibility changes of siderite as well as of additional minerals irradiated with accelerated electrons only to the surface layer is a characteristic feature of the process mentioned.

5. CONCLUSION

Irradiation of siderite with accelerated electrons allows us to increase substantially its magnetic susceptibility. This phenomenon is conditioned by thermic decomposition which arises at intensive irradiation of siderite with a sufficient energy dose of accelerated electrons at the access of air. A ferromagnetic layer, which can be produced by this process on the surface of siderite grains, improves magnetic properties of siderite to such a degree which allows its effective treatment in a weak magnetic field.

REFERENCES


Florek I., Murova I., (1993), Modyfikacja magnetycznych własności syderytu szybkimi elektronami, Physicochemical Problems of Mineral Processing, 27, s. 145-149 (English text)

Na podstawie wiedzy o właściwościach jonizacyjnych szybkich elektronów zbadano warunki ich użycia do modyfikacji właściwości magnetycznych syderytu. Badania wykazały korzystny wpływ napromieniowania szybkimi elektronami na podatność magnetyczną syderytu, która po napromieniowaniu wzrosła dwudziestokrotnie. Wzrost podatności magnetycznej zachodzi w wyniku termicznego rozkładu syderytu i tworzenia się nowych faz ferromagnetycznych na jego powierzchni. Wielkości dawk promieniowania i warunki utleniania syderytu są decydującymi czynnikami tego procesu.