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#### ONTOGENY OF HALITE INDIVIDUALS AND AGGREGATES FROM HIGH-GRADE IRON ORES OF KRYVYI RIH BASIN

Results of ontogenetic studies of halite referring to harmful mineral impurities of high-grade iron ores of Kryvyi Rih basin are given. The features of nucleation, growth, and change in halite crystals and aggregates are characterized. It is noted that a comprehensive mineralogical, including ontogenetic, study of halite is necessary for the development of optimal technologies for minimizing alkali content in the saleable sinter ore of Kryvyi Rih basin.

General information. Halite refers to conststant mineral components of high-grade iron ores extracted by the mines of the Saksaganskyi iron ore district of Kryvyi Rih basin [6]. It is a harmful mineral component in ores. In connection with this the content of sodium in the composition of iron ore is regulated on the world market: cumulative quantity of sodium and potassium oxides  $(Na_2O+K_2O)$  must not exceed 0.1 mass.%.

High-grade iron ores from all the mines of the Kryvbas contain high concentration of alkali, mainly sodium, and potassiumin in a lesser degree. Over the last 50 years, the content of Na<sub>2</sub>O+K<sub>2</sub>O in ores is constantly increasing with the increase in depths of mining (currently 1300-1500 m). At the beginning of 2015 this figure amounted to an average of 0.35 mass.% (ranging from less than 0.1 to 1.0 mass.%). This explains the **relevance** of mineralogical and chemical research, technological tests, aimed at *minimizing* the alkali content in the ores to allowable showings.

The aim of the work was to study the conditions for the nucleation, growth and changes in individuals of halite as a main alkali bearer in the composition of high-grade iron ores in Kryvbas.

37 salt samples represented by individuals and aggregates of halite formed on the surface of the saleable sinter ore stockpile of "Rodina" Mine

have been used as **initial raw material**. The mine selection was due to the highest halogenides content, mainly of halite, in its ore.

**Research methods**: crystallomorphological, ontogenic – macroscopic and using a binocular microscope.

Results and their discussion. Results of crystallomorphological and ontogenetic studies of individuals and aggregates of halite have allowed determining the peculiarities of their nucleateon, growth and change on the surface and in the volume of saleable ore mass.

**The nucleation** of individuals and aggregates of halite occurred: 1) spontaneously in suspension; 2) forcedly on the surface of crystals and aggregates of halite of earlier generation; 3) forcedly at the surface of the ore particles composed mainly of hematite and quartz [1, 2, 4, 7].

In the first case, outlines of seed individuals having hexahedral shape ranging from 0.01 to 0.1 mm have been noticed in the central parts of large (5.1 mm or more) crystals. Due to the fact that further crystal growth occurred mainly by uniform sedimentation of sodium and chloride ions on the surface of all faces, the crystal growth zone of equal width have been recorded (Fig. 1).

Upon reaching the size of 0.5-1 mm crystals sank to the ore substrate, and their further growth

took place in interaction with it, as well as with other halite crystals and aggregates.

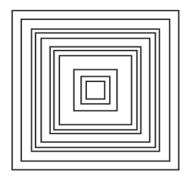


Fig. 1. A halite crystal of about 0.5 mm in size, spontaneously nucleated in highly mineralized mine water.

Forced nucleation of individuals of halite on the surface of the crystals or aggregates of earlier generations [1, 2, 4] happens repeatedly. Usually it takes place in connection with the input of new portions of highly mineralized mine water with new batches of ore material, or in connection with the leaking of the mine water pumping systems. Nucleation micro-crystals are initially formed individually, and after a while, they are trapped by common growth areas with a large crystal of earlier generation, as shown in Fig. 2.

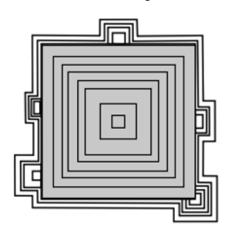


Fig. 2. The nucleation of small halite crystals on the surface of a large crystal of earlier generation.

The length of the edges of the crystal-substrate is about 0.4 mm.

Forced halite crystal nucleation is also observed on the partially dissolved (after rains or dust control measures in ore stockpile) surface of the previously formed crystals (Fig. 3) or on the surface of mechanically destroyed crystals and aggregates of halite [1, 2 4, 7] of earlier generations (Fig. 4).

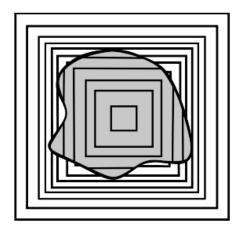


Fig. 3. The nucleation of a halite crystal on the surface of a semisolved crystal of earlier generation.

The length of the formed crystal edge is about 0.6 mm.

In most cases the orienting influence of the substrate on the nucleating halite microcrystals takes place.

There were manifestations of two mechanisms of induced nucleation of halite crystals on the surface of the ore.

- 1. The nucleation on the surface of suspended particles of ore, the size of which, according to the microscopic observations, did not exceed 0.2 mm. In this case (Fig. 5) ore particle became overgrown with seed crystals of halite. Upon reaching the aggregate size of 0.5-1 mm it sank on the substrate, the further growth of the halite crystals occurred in the interaction with the substrate [2, 4, 5, 7].
- 2. The nucleation on the surface of the ore substrate. Formation of seed crystals occurred at the initial stage of water evaporation (Fig. 6). With increasing intensity of this process the size of the crystal increases, their growth took place in the

interaction. After drying, the ore substrate was covered with a crust of halite crystals ranging from 0.1 to 10 mm.

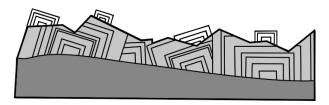


Fig. 4. The nucleation of halite crystals on the surface of mechanically destroyed individuals of an earlier generation.

Edge length of newly formed microcrystals is 0.05-0.1 mm.

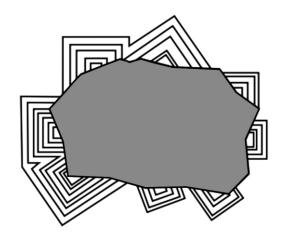


Fig. 5. The nucleation of halite crystals on a fine (about 0.2 mm in maximum measurement) ore particle in suspension.

The size of halite individuals is 0.02-0.05 mm.



Fig. 6. The nucleation of halite crystals on the surface of the ore substrate.

The edge length of halite crystals is 0.1-0.2 mm.

Crystal *growth* takes place as well on halite seeds suspended in the feed solution, and after precipitation on the ore substrate. As it was shown by the results of crystallomorphological studies, the crystal growth takes place with formation of holohedral, less often of edge and vertex skeletal forms [1, 2, 4, 5, 7, 8].

The growth of holohedral crystal is realized by depositing ions Na<sup>+</sup> and Cl<sup>-</sup> on the surfaces of faces by flat or spiral layers [1, 2, 4]. Manifestations of both growth mechanisms are observed on the surface of the studied halite crystals. In the case of growth by flat layers the initial crystal seed of the layer (Generation Point) usually joins in with the apex of the crystal. Its joining in with an edge is less energetically advantageous, and therefore less likely to happen, and its joining in with a face is even less likely to be realized [4]. All subsequent ions of this layer are deposited in dihedral angles formed between the surface of the previous layer and the initial crystal nuclei of the forming layer. The layer growth continues until it is full. With the growth by spiral layers, dislocation in the previously formed layers have the role of generating points; faces growth occurs according to a screw way.

Crystal growth occurre in the conditions of changes in the growth-supporting environment: there are changes in the weather conditions, solution concentration, and its periodical turbidity take place. Mechanical impurities in halite crystals are associated with the latter. The rhythmic repetition of turbidity of mine water and deposition of particles in the process of crystal growth has led to the visualization of their zoning [1, 2, 4]. Zonal distribution of nanoparticles of dispersed hematite and kaolinite in crystals is the most common (Fig. 7).

High concentration of salt in the mine water or high crystallization rate resulted in the formation of skeletal crystals of halite such as edge ones, less of vertex ones [4, 8]. This was due to the constant formation of new primary crystal seeds of layers (the generation points) at the apexes and along the edges of the crystal, and delay in the filling of the central parts of faces (Fig. 8).

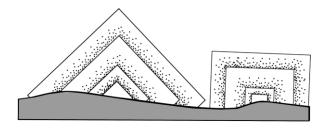


Fig. 7. The zonal structure of halite crystals caused by rhythmic mine water turbidity and deposition of nanoparticles of dispersed hematite on the faces of growing crystals.

Edge length of a larger crystal is 2.6 mm.

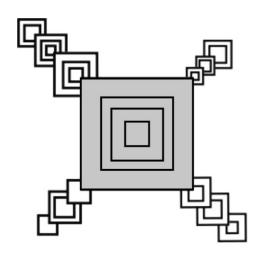


Fig. 8. The structure of the edge crystal of halite in section through its center along the axis of fourfold simmetry on a plane, that is perpendicular to the faces of hexahedron.

The holohedral core edge length is approximately 0.3 mm; fine crystals edge length is from 0.03 to 0.1 mm.

Changing the halite crystals and aggregates in high-grade ores occurs for two main reasons: the mechanical action (brittle deformations) and dissolving [1, 2, 4, 7]. In the first case, halite crystals and aggregates typically experienced brittle deformation due to repeated overloading of the ore material. This resulted in their partial (Fig. 9) or complete destruction.

As mentioned above, the delivery of new portions of mine water, precipitations resulted in lower concentrations of salts in the feed solution. It causes partial or complete dissolution of the formed crystals (Fig. 10).



Fig. 9. The aggregate of halite crystals with mechanically destroyed surface.

Halite individuals size is from 1 to 3 mm.



Fig. 10. The aggregate of halite crystals with surface subjected to dissolution.

Halite individuals size is from 1 to 3 mm.

At later stages, mechanically destroyed, or partially dissolved halite crystals could serve as seeds for the nucleation of crystals of new generations, as it is shown in Fig. 3, 4.

#### Conclusions

- 1. Halite is a permanent mineral component of high-grade iron ores of Kryvyi Rih basin; it refers to the harmful impurities in iron ore. Its content in ores is 3-4 times higher than it is acceptable by the world market requirements.
- 2. Increased salinity mine waters with the content of soluble sodium compounds in terms of Na<sub>2</sub>O in averages 0.35 mass.%, in some cases makes up to 1.0 mass.%, are the source of the halite formation.
- 3. The nucleation of halite crystals takes place spontaneously in suspension in the volume of feed solution or is stimulated on the surface of halite crystals of earlier generations, or on the surface of the ore particles. The growth is realized to form holohedral, less often edge and vertex skeletal forms. Alteration and destruction of halite crystals usually takes place under mechanical influence or

due to dissolution. Destroyed or partially dissolved halite crystals are often seeds for the nucleation of new generations of crystals.

необходимо в связи с разработкой оптимальной технологии снижения содержания щелочей в составе товарных агломерационных руд Криворожского бассейна.

4. Comprehensive mineralogical studying of halite, including its crystals and aggregates ontogeny [3] is necessary in terms of the development of optimal technology for minimizing alkali content in the saleable sinter ore of Kryvyi Rih basin.

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# БЕРЕЗА Д.В., ЄВТЄХОВ В.Д., ЄВТЄХОВА А.В., ДЕМЧЕНКО О.С., ГЕОРГІЄВА О.М. Онтогенія індивідів і агрегатів галіту з багатих залізних руд Криворізького басейну.

Резюме. Галіт постійно присутній у багатих залізних рудах Криворізького басейну. Він відноситься до шкідливих мінеральних домішок залізних руд, у зв'язку з чим вивчення його мінеральної природи, умов утворення, розподілу в рудних покладах необхідно для оцінки якості руд, їх вартості тощо. Вміст галіту в складі руд Кривбасу в 3-4 рази вищий від допустимого за вимогами світового ринку. Джерело утворення галіту — підвищеної солоності шахтні води, в яких вміст розчинних сполук натрію в перерахунку на №2О коливається від менше 0,1 до 1,0 мас.%, в середньому становить 0,35 мас.%. За результатами онтогенічних досліджень, зародження кристалів галіту відбувається самовільно у зваженому стані в об'ємі живлючого розчину або примусово на поверхні кристалів галіту ранніх генерацій та на поверхні рудних частинок. Рост кристалів реалізується шляхом утворенням повногранних, значно рідше реберних і вершинних скелетних форм. Зміни та руйнування кристалів галіту, зазвичай, відбувається під дією ме-

ханічних навантажень або внаслідок розчинення. Зруйновані або частково розчинені кристали галіту можуть бути затравками при зародженні кристалів нових генерацій. Всебічне мінералогічне, в тому числі онтогенічне вивчення кристалів і агрегатів галіту необхідне для розробки оптимальної технології зниження вмісту лугів у складі товарних агломераційних руд Криворізького басейну.

**Ключові слова**: залізисто-кремниста формація, Криворізький басейн, багаті залізні руди, галіт, онтогенія галіту.

## БЕРЕЗА Д.В., ЕВТЕХОВ В.Д., ЕВТЕХОВА А.В., ДЕМЧЕНКО О.С., ГЕОРГИЕВА Е.П. Онтогения индивидов и агрегатов галита из богатых железных руд Криворожского бассейна.

**Резюме**. Галит относится к постоянным минеральным компонентам богатых железных руд Криворожского бассейна. Он является вредной минеральной примесью руд, связи с чем количество галита, как и других щелочь-содержащих минералов в рудах регламентируется. По нормативам мирового рынка, суммарное количество оксидов натрия и калия ( $Na_2O+K_2O$ ) в составе железорудного сырья не должно превышать 0,1 мас.%.

Богатые железные руды всех шахт Кривбасса отличаются повышенным содержанием оксидов щелочей,— главным образом, натрия, в значительно меньшем количестве калия. В начале 2016 г. этот показатель в среднем составил 0,35 мас.% (колебания от 0,1 до 1,0 мас.%). Этим обусловлена актуальность минералогических и химических исследований, технологических испытаний, направленных на снижение содержания щелочей в составе руд до приемлемых показателей.

Целью авторов было изучение условий зарождения, роста и изменения индивидов галита как главного носителя щелочей в составе богатых железных руд Кривбасса. В качестве исходного материала использовались 37 проб солей, представленных индивидами и агрегатами галита, которые образовались на поверхности рудной массы и вокруг склада товарной агломерационной руды шахты «Родина». Выбор шахты был обусловлен наиболее высоким содержанием галогенидов, главным образом, галита в составе ее товарной руды.

Результаты кристалломорфологических и онтогенических исследований индивидов и агрегатов галита позволили определить особенности их зарождения, роста и изменения на поверхности и в объеме товарной рудной массы.

Зарождение кристаллов происходит: 1) самопроизвольно во взвешенном состоянии; 2) вынужденно на поверхности кристаллов и агрегатов галита более ранней генерации; 3) вынужденно на поверхности частиц руды, сложенных, главным образом, гематитом и кварцем.

Рост кристаллов происходит как на зародышах во взвешенном состоянии, так и после их осаждения на рудный субстрат. Обычно образуются полногранные, значительно реже реберные и вершинные скелетные кристаллы. Периодическое взмучивание шахтной воды и осаждение наночастиц гематита и каолинита на поверхности растущих кристаллов галита является причиной визуализации их зональности.

Изменение и разрушение кристаллов галита обычно происходит под действием механических нагрузок или вследствие растворения. Разрушенные или частично растворенные кристаллы часто служат затравками для зарождающихся кристаллов галита новых генераций.

Всестороннее минералогическое, в том числе онтогеническое изучение галита необходимо для разработки оптимальной технологии снижения содержания щелочей в составе товарных агломерационных руд Криворожского бассейна.

**Ключевые слова**: железисто-кремнистая формация, Криворожский бассейн, богатые железные руды, галит, онтогения галита.

### BEREZA D.V., EVTEKHOV V.D., EVTEKHOVA A.V., DEMCHENKO O.S., GEORGIIEVA E.P. Ontogeny of halite individuals and aggregates from high-grade iron ores of Kryvyi Rih basin.

Summary. Halite is constantly present in high-grade iron ores in Kryvyi Rih basin. It refers to harmful mineral impurities in iron ores, and therefore, the study of its mineral nature, formation conditions, distribution in ore deposits is necessary to assess ore quality, cost, etc. Halite content in Kryvbas ores is 3-4 times higher than allowable one by requirements of the global market. Halite formation is caused by salinity of mine waters in which the content of soluble sodium compounds in terms of Na<sub>2</sub>O ranges from less than 0.1 to 1.0 mass.%, the average is 0.35 mass.%. After the results of ontogenetic studies halite crystal nucleation occurs spontaneously in suspension in the volume of the feed solution or forcedly at the surface of the halite crystals of early generations and at the surface of ore particles. Crystal growth is realized by forming holohedral, less often edge and vertex skeletal forms. Alteration and destruction of halite crystals usually takes place under the influence of mechanical loads or by dissolution. Destroyed or partially dissolved, halite crystals may become seeds for new generations of crystals. Comprehensive mineralogical, including ontogenetic, study of halite crystals and aggregates is necessary for developing optimal technologies for minimizing alkali content in seleable sinter ores of Kryvyi Rih basin.

**Key words:** banded iron formation, Kryvyi Rih basin, high-grade iron ores, halite, halite ontogeny.

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