Hydrohalite of salt waste piles of the Verkhnekamsky deposit (Ural, Russia)

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In the winter period in vicinities of technological salt waste piles at low-temperature cristallisation the thick sediments of hydrohalite are formed. The sizes and form of crystals depend on temperature and density of the brines.

In the course of mining and processing potassium salts at the Verkhnekamsky deposit, flat-topped salt waste piles form within a short period of time. On account of the genetic features of the ores, and the technological parameters of the production of potassium chloride, more than 95% of the dumps poured on the surface is composed of water-soluble minerals (first and foremost halite). The salt dumps occupy a total area of more than 450 hectares on the territory of the deposit. More than 2.5 million cubic meters of depositions settle on the dumps annually which results in one million tons of dissolved matter being washed away from the dumps. The leaking brines collect in special reservoirs where the mineral matter settles along their sides and bottoms. Intensive formation of halite building up a dense coarse-grained crust on the bottom, and a loose porous aggregate of fine grains along the sides occurs in the summer. On hot days, crater like "little boats" of halite form on the surface of the brine which, when immersed, form a crust on the bottom.

Settlement of the mineral phase also occurs in the winter period. The brine becomes supercooled, their physical and chemical parameters change (table 1) and coarse aggregates and growthes of monoclinic crystals of hydrohalite $NaCl\bullet 2H_2O$, that have hexagonal contours, form on the reservoir and stream bottoms. The sizes and habits of the newly formed crystals vary greatly and depend on the physicochemical properties of the brine on this area. On stream bottoms, where higher temperatures (from 0° to -3° C) and an active hydrodynamic regime are characteristic of the brine, coarse (up to 1.5 to 2 cm) isometric transparent individs crystallize which have uniform developed faces (100), (110), (111) and ($\bar{1}$11). As the brine moves further away from the place of exit under the waste pile, the speed of the stream decelerates and the temperature of the liquid falls proportionately. This results in a change of the physicochemical properties of the brine, and as a result, to a change in the sizes and shapes of the formed crystals. As the temperature of the brine falls, the area of first and second pinacoids increases and the area of the prism (111) and ($\bar{1}$11) decreases. Elongated prismatic and columnar crystals form, which reach up to 10 cm in length, and from 0.5 to 0.8 cm in width. Meanwhile, the size of separate individs decreases with the drop in temperature. In greatly supercooled brines (from to -10° to -12° C) a large number of acicular crystals from 1.5 to 2 cm in length have been found at the bottom deposits. The nature of individ cohesion is fragile — the aggregates can be easily damaged if strained.

When the brine undergoes abrupt supercooling, coarse (up to 6 cm) transparent crystals grow in shallow areas within a 24 hour period. The crystals are flattened on (100), with faces (100), (010), (111), ($\bar{1}$11) and good visible growth zones. Re-entering angles are observed on separate individs, indicating a possible twinning along (100). A chemical analysis of these crystals showed that the crystals contain the following main components: Na — 24.45%, Cl — 37.22%, H_2O — 38.33%. Additionally, the presence of a small quantity of sulfate ions and calcium were also detected (evidently from numerous liquid-gaseous inclusions in the brine).

Table 1
Differences of physical and chemical parameters of summer and winter brines

Parameter	Summer brines	Winter brines
Density, g/l	1.185 — 1.190	1.205 — 1.210
Eh, mV	70	84
pH	6.24	6.31
Cl^-, mg/l	$177.25*10^3$	$161.7*10^3$
$(SO_4)^{2-}$, mg/l	2575	5367
Na^+, mg/l	$114.43*10^3$	$105.73*10^3$
K^+, mg/l	320	220
Ca^{2+}, mg/l	1385.8	1293.4
Mg^{2+}, mg/l	89.62	123.7

Individual snowflakes that fall in saturated supercooled brine become the centers of crystallization and cause intensive settlement of the hydrohalite. At the same time, a large number of fine isometric crystals form, growing over coarser crystals from earlier settlements. The result is fragile bud-like or cluster aggregates with coarse individs in the center and fine individs along the periphery.

Studying of hydrohalite is difficult because it is only stable at below freezing temperatures. As the crystal is gradually warmed, it surface begins to cover with cloudy (due to the large amount of fine cubic halite crystal) drops of brine, then it slowly begins to be replaced by white fine-crystalline halite with a small amount of excreted liquid solution. The loss of water happens gradually, and at below freezing temperatures. In this case, the crystals of the hydrohalite are replaced by dry white fine-crystalline halite.