Modeling the interaction of mine brines with chloride minerals of potassium-magnesium deposits

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Abstract. The article is devoted to study of dynamics of saturation degree of suprasalt brines with respect to major chloride minerals of salt strata in the initial phase of an accident related to discontinuity of waterproof stratum in the mine of the Verkhnekamskoe salt deposit (Berezniki-3 mine, 1986). Physicochemical modeling has showed that the brines discharged into mine are in equilibrium with halite during all period of observation. At the same time, their degree of saturation with respect to sylvite and carnallite regularly decreases with the increase in inflow of the suprasalt Cl-Na brines. The initial stage of suprasalt brine penetration into mine is characterized by an increase in the saturation degree with respect to the considered chloride minerals, which is showed on the chart presented in the article. However, there are brines oversaturated with respect to halite, which occurs over a brief period. In contrast to the mine brines of different genesis being in equilibrium or close to equilibrium with sylvite, saturation index (SI) for this mineral decreases in the suprasalt brine. This allows one to recommend the use of this parameter in the study of the mine brines to timely detect suprasalt brines entering the mine.

1. Introduction
The Verkhnekamskoe salt deposit (VKSD) is located on the left bank of the Kama river within Perm Krai. By its tectonic nature, the deposit is related to Solikamsk depression of the Fore-Urals Trough. The deposit can be characterized as a multimineral one: sylvinite (raw material for potash fertilizer production), carnallite (artificial carnallite production in magnesium industry) and rock salt are mined there. VKSD is one of the biggest deposits in the world, with 30 % of world potash ore. Deposit salt stratum is of 8 100 km$^2$, the area of potash deposit is 3 750 km$^2$ [1]. The deposit is developed by underground mining method, the mines being 100-500 m in depth.

VKSD has solid (more than 500 m) salt strata with the layers (from bottom to top) of underlying rock salt (URS) of 320-400 m, potash deposit (70-100 m) and covering rock salt (CRS) (20 m). Salt stratum is underlied with clay-anhydrite deposits of 200-220 m and covered with salt-marly (SMS), terrigenous-carbonate (TCS) and speckled (SS) strata of the Ufimian strata of the lower Permian (figure 1). A set of salts is related to the Iren horizon of the Kungurian strata of the lower Permian System. Sylvinite (with average thickness of 17.5 m) and carnallite (with average thickness of 54 m) zones comprise potash deposit [1].

The lens-shaped salt strata of the deposit act as a regional aquaclude dividing suprasalt and subsalt waters, the first being fresh, mineralized waters and brines, while the second being highly-mineralized brines. Waters of brine horizon come out from the holes in some areas at the top of salt strata or near...
it. It has been noted that these waters have Cl-Na composition, and their mineralization achieves 320 g/L [1].

The deposit mines are very often characterized by the technogenic brines - condensate and stowage brines. Salt deposit contains some amount of post-sedimentation (intrasalt) brines. Condensate brines are caused by the interaction of moisture from air and salt rocks. In the mines these brines are everywhere represented by the puddles, small lakes in the degradations and downpour from the cover. Stowage brines are represented by the liquid phase entering the mines together with the salt-processing waste applied in stowing worked-out area and being pressed while solidifying stowage material in mines.

Waterproof stratum (WPS) is defined as a stratum of rocks the upper border of which is the first rock salt layer of intermediate zone (IZ) of salt-marl strata and the lower border of which is the cover of the salt deposit's upper layer being processed (figure 1). With discontinuity of WPS due to natural factors or mining works, the suprasalt waters interact with the rocks of salt deposit and wash away the cracks, which results in the increase in water inflow in the mines and mine flooding. WPS discontinuity and the breakthrough of the suprasalt stratum groundwater have led to the flooding of two VKSD mines (Berezniki-3 mine, 1986; Berezniki-1 mine, 2006) and an accident in Solikamsk-2 mine (2014). WPS outbreaks together with further solution of salt stratum in the areas of suprasalt waters discharging in a mine are accompanied with the sinkholes on the surface.

In case of an accident, the highly-mineralized suprasalt brines of CS leaching are the first to be discharged in the mines. Mining work safety is closely connected with fast detection of these brines among the other mine brines described above.

2. Objects and methods

The research in this paper is supported by the evaluation of saturation degree of accident causing suprasalt brines with respect to chloride minerals of VKSD salt strata on the basis of saturation index (SI) identification. Due to highly-mineralized brines, the activity coefficients in the paper were identified with the Pitzer model [3-6]. Being in agreement with the experimental data, this model is widely used in the papers of the scientists [7, 8].

To calculate brine equilibrium with chloride minerals (halite NaCl, sylvite KCl and carnallite KMgCl$_3$·6H$_2$O), PHREEQC code was applied [9]. Physicochemical modeling was done with standard atmospheric pressure at 10°C brine temperature.

In our studies of accident causing suprasalt brines connected with the WPS discontinuity, we turned to the accident happened in Berezniki-3 mine in 1986, which was described in detail in the works published [2, 10, 11]. In the present research, we analyzed some measurement data provided in these works, namely, the data on hydrochemical sampling of brines in one of the deposit mines regarding the major ions, Br, pH value and density.

Two layers of sylvinite zone ("AB" and "Red-II") till 1979 and later layer "Red-II" were worked out in a mine located at the center of VKSD southern part. On the 11th of January, 1986, brines in the form of separate small streams were discovered from the cover of chamber № 50 of the western half block of the mine. At the same time the brines appeared in the cover of chamber № 52. For the next several days the brines started to flow in the covers of the other chambers as well. Approximate evaluation showed that at the initial stage the overall inflow in a mine was about 10 m$^3$/hour. On the 6th of February summarized inflow of brines was about 60 m$^3$/hour, on the 22nd of February – 100 m$^3$/hour. On the 1st of March the inflow was 150 m$^3$/hour, in the morning of the 9th of March it was 500 m$^3$/hour. In the evening of the 9th of March the inflow increased up to 5,000 m$^3$/hour and increased further. By the end of June all worked-out area of Berezniki-3 mine field was flooded with suprasalt waters, with their calculated overall volume being about 15 ml. m$^3$ [1]. On the night of July 23, 1986, six and a half months after the brine's streams had been found in the cover of the mine, a sinkhole in the ground formed over the place of suprasalt groundwaters breakthrough. The thickness of the suprasalt stratum in the breakthrough area consisting of SS, TCS and SMS is about 350 m (Figure 1). Below, there is covering salt (CS) of 20 m in thickness and productive strata of 70 m in
thickness with interlayering rock salt, sylvinite and carnallite. Underlying salt is up to 400 m in thickness. The sinkhole was formed in the area with WPS of more than 100 m in thickness.

Figure 1. Geological strip log 143g (Berezniki-3 mine).

3. Results of the research

Table and Figure 2 show the dynamics in the composition components of suprasalt brines inflowing the chamber 52 of Berezniki-2 mine from January 11, 1986 till March 08, 1986. The brines were sampled for the chemical analysis from 1 to 6 times within 24 hours. “Jump” in the chart from January 21, 1986 till February 01, 1986 corresponds to the lack of observation data.

Table. Changes in composition components of suprasalt brines entering the mines from January 11, 1986 till March 08, 1986, g/L, density ρ (g/cm³).

| Observation period | N  | pH  | ρ  | Cl⁻  | SO₄²⁻  | HCO₃⁻  | Br⁻  | Na⁺  | K⁺  | Mg²⁺  | Ca²⁺  | TDS  |
|-------------------|----|-----|----|------|--------|--------|------|------|-----|-------|-------|------|
| 11 Jan – 12 Jan, Cl-Mg type, Q = 10 m³/h | 5.70 | 1.282 | 258.86 | 0.49 | 0.33 | 4.26 | 12.00 | 8.26 | 69.92 | 11.50 | 365.62 |
| Beginning         | 5.10 | 1.260 | 278.36 | 0.63 | 0.18 | 1.96 | 27.40 | 18.10 | 70.98 | 8.00  | 405.61 |
| Ending            | 5.35 | 1.267 | 263.88 | 0.57 | 0.23 | 2.76 | 17.86 | 15.15 | 70.17 | 9.08  | 379.71 |
| Average           | 3    |      |        |      |       |      |       |      |      |       |       |      |
| 13 Jan – 21 Jan, Cl-Na-Mg type, Q = 100 m³/h by 22 Jan | 5.75 | 1.230 | 214.53 | 1.72 | 0.16 | 0.97 | 58.30 | 32.40 | 29.49 | 6.25  | 343.82 |
| Beginning         | 6.24 | 1.216 | 207.44 | 1.73 | 0.15 | 0.73 | 73.19 | 28.00 | 21.58 | 4.50  | 337.32 |
| Ending            | 6.14 | 1.222 | 210.61 | 1.60 | 0.14 | 0.77 | 69.59 | 30.24 | 23.66 | 5.05  | 341.67 |
| Average           | 23   |      |        |      |       |      |       |      |      |       |       |      |
| 01 Feb – 08 Mart, Cl-Na type, Q = 5000 m³/h by 09 Mart | 6.20 | 1.210 | 202.12 | 2.30 | 0.15 | 0.51 | 90.73 | 19.05 | 13.98 | 3.50  | 332.34 |
| Beginning         | 6.50 | 1.204 | 195.03 | 3.86 | 0.18 | 0.20 | 114.72 | 6.25  | 4.26  | 1.75  | 326.25 |
| Ending            | 6.54 | 1.206 | 195.39 | 3.42 | 0.18 | 0.24 | 108.79 | 9.40  | 6.07  | 2.33  | 325.82 |
| Average           | 93   |      |        |      |       |      |       |      |      |       |       |      |
In the initial period of the accident (January 11-12) the discharging brines were characterized with Cl-Mg composition. Their average density was 1.267 g/cm$^3$, and mineralization was 380 g/L. The 12th of January saw the brines with the highest concentration of chlorides and mineralization (405 g/L) for the period in question. It is possible that the first streams of the brines in the cover of the mine were followed by the initial cavity of solution in carnallite zone (CZ in figure 1) due to the inflow of suprasalt brines. Here the brines were enriched with Mg$^{2+}$ in their interaction with carnallite, Cl$^-$ concentration together with their mineralization and density increased. With further development of the crack (damage) in waterproof stratum (WPS), the brines from the sinkhole flew into the mines.

With the expansion of cross-section area of discharge channels to mines and with the increase in inflow of suprasalt waters with Cl-Na composition, the brines turn into Cl Na-Mg type, on average their mineralization changes up to 342 g/L, density - 1.222 g/cm$^3$ (January 13-21). Later (February 1 - March 8) the mines receive Cl-Na brines typical for the lower part of SMS, with average mineralization of 326 g/L, density of 1.206 g/cm$^3$.

Figure 2. Dynamics of composition components of suprasalt brines discharging in mines (accident in Berezniki-3 mine in 1986).

The chart in figure 3 illustrates changes in saturation degree of suprasalt brines entering the mines with respect to the considered chloride minerals. The chart shows that the inflowing brines over the whole observation period are characterized with the equilibrium state with respect to halite. At the same time, in the initial period of the accident (January 12) the brines oversaturated with respect to halite (SI$_{\text{halite}} = 0.46$), sylvite (SI$_{\text{sylvite}} = 0.14$) and equilibrium with carnallite (SI$_{\text{carnallite}} = 0$) are discharged for a short period of time. Some samples of post-sedimentation (intrarsalt) brines met in the mine’s cover in the border of carnallite and sylvinate zones (“B”-“V” layers) are noted to be maximum close to chloride minerals by the chemical composition and saturation degree. For example, the brine of sample № 1407 (Solikamsk-2 mine, 2012) is characterized by 407 g/L mineralization, 1.273 g/cm$^3$ density, content (g/L): Cl$^-$ - 269.52; Na$^+$ - 24.86; K$^+$ - 18.23; Mg$^{2+}$ - 60.60. Degree of brine saturation (SI) to chloride minerals is: with respect to halite 0.31; to sylvite 0.06; to carnallite“-0.30”. Thus, we can identify the initial cavity of solution in carnallite zone, where inflowing Cl-Na brines are enriched with Mg$^{2+}$ and Cl$^-$ and reach equilibrium with respect to carnallite. With the development of WPS damage before the mine’s cover these brines are first to discharge. G.V. Beltyukov [2] holds the same opinion. He suggests that "paleokarst cavities filled with the brines and hydraulically connected with the suprasalt waters” are the initial sources of brines inflow.
Figure 3. Dynamics of saturation degree of suprasalt brines entering the Berezniki-3 mine with respect to chloride minerals from January 11, 1986 till March 08, 1986. Chamber № 52.

With the increase in inflow of suprasalt Cl-Na brines, their saturation degree with respect to sylvite and carnallite regularly decreases (see figure 3). In observation period corresponding to the discharge of Cl-Na-Mg brines in the mines (January 13-21), saturation degree (SI) with respect to sylvite changed from -.0.11" to ".-0.22" (average value ".-0.17"), with respect to carnallite from "-1.88" to "-.2.25" (average value ".-2.12"). With the inflow of Cl-Na brines (1 February - 8 March) saturation degree with respect to sylvite changed from "-0.44" to "-.1.00" (average value ".-0.83"), with respect to carnallite from "-2.75" to "-3.95" (average value ".-3.66"). In his paper A.I. Kudryashov [1] points out that by 10.03.1986 more than 250 thousand m$^3$ of "maximum salt saturated solutions" flew into Berezniki-3 mine. Here, considering the above-mentioned facts, we should note: solutions saturated with respect to halite (but undersaturated with respect to sylvite and carnallite).

Analysis of 324 brine samples of different genesis taken in VKSD mines in 2011-2014 shows that mine brines are in equilibrium or in close equilibrium with respect to halite and sylvite [12]. For example, saturation index SI by sylvite ranges between "-0.2" and "0.2" with the prevalence (94 % of samples) of the values from "-0.11" to "0.18". Due to genesis and chemical composition the brines of the mine differ in their saturation degree with respect to carnallite. The present paper shows that in comparison with the mine brines suprasalt Cl-Na brines (the ones which penetration into the mine is caused by WPS discontinuity) are less saturated with respect to sylvite. Therefor, it is advisable to take into account the saturation degree with respect to sylvite expressed in SI, when studying the mine brines, to improve safety in mining.

4. Conclusion
Suprasalt Cl-Na brines connected with leaching of CS and salt layers in the lower part of SMS are in equilibrium with respect to halite. When the suprasalt brines flow into Berezniki-3 mines due to WPS discontinuity, in the initial stage their interaction with carnallite in productive stratum increases the saturation degree with respect to sylvite and carnallite. In this case the brines have Cl Na-Mg composition. Brief inflow of Cl-Mg brines being in equilibrium with carnallite and oversaturated with respect to halite is likely to be connected with the formation of the initial solution cavity in carnallite zone, which development follows the first accident brines in the mine's cover.

With the increase in inflow rate in the mines, the discharging brines change their chemical type from Cl Na-Mg to Cl-Na. Their composition corresponds to suprasalt brines of the SMS lower part; solution of carnallite zone sediments has the minimum impact on the composition.
In comparison with the mine brines of different genesis, suprasalt brines are undersaturated with respect to sylvite.

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