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Development of a New Technology for Complex Utilization of Mineral Resources of the Kara-Bogaz-Gol (Turkmenistan) under Present Conditions

H13/2006

Principal Investigator: Prof. Boris Krumgalz
Collaborators: Prof. A. M. Khodjamamedov
and Dr. N.N. Kazantseva

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#	SUBJECT	Page
	COVER PAGE	1
I.	CONTENT	2
II.	INTRODUCTION	3
III.	SCIENTIFIC SUMMARY & EXPERIMENTAL PART	4
1.	Sampling places	4
2.	The composition of Kara-Bogaz-Gol surface brines	4
3.	Drainage of Caspian Sea water to Kara-Bogaz-Gol	5
4.	Solar evaporation of the Kara-Bogaz-Gol surface brine	5
5.	Experiment on solar evaporation of surface brine	6
6.	Results and discussion	6
7.	The development of the dynamic model for natural water evaporation	9
8.	Thermodynamic model for water evaporation and mineral precipitation from natural brines	12
9.	Results of thermodynamic modeling for water evaporation and mineral precipitation from	14
IV.	DEVELOPMENT OF A TECHNOLOGY SCHEME FOR COMPLEX PROCESSING OF SURFACE BITTERNS OF KARA-BOGAZ-GOL GULF	14
1.	First variant	14
2.	Second variant	15
3.	Crystallization of mirabilite and the evaporation of mirabilite mother brine	15
4.	Development of technology for production of potassium sulfate from surface bitterns	18
5.	Development of technology for production of magnesium chlorate from surface bitterns	20
V.	CONCLUSIONS	20
VI.	RECOMMENDATIONS FOR INDUSTRIAL IMPLEMENTATION OF THE DEVELOPED TECHNOLOGY	21
VII.	REFERENCES	22
VIII.	TABLES	25
IX.	FIGURES	33
X.	APPENDIX	35
XI.	MANAGERIAL ISSUES	38
XII.	COLLABORATION AND TRAVEL	38
XIII.	ACKNOWLEDGMENT	38

II. INTRODUCTION

The unique Kara-Bogaz-Gol Gulf basin is the largest salt basin on Earth. The Gulf is a renewable natural source of raw materials for the industrial production of sulfates and chlorides of sodium, magnesium, potassium, boron compounds, bromine and some rare elements. The mineral resources are present in surface brine, in second salt level brine, in solid salt precipitations and in overflow brines from active plants. The Kara-Bogaz-Gol salt deposits are of a marine type. The surface brines contain twice the potassium and microelements than the buried brines.

The Kara-Bogaz-Gol Gulf is connected to the Caspian Sea by eleven kilometers strait. The composition of surface brines is determined by the fluctuations of the Caspian Sea level. The maximum area of the Gulf reaches about 20 km^2. In 1980, after complete damming the strait, the surface brines dried during 2.5 years. Later, in the middle of eighties, in order to reanimate the Gulf, 11 pipes were installed in the dam to draw seawater from the Caspian Sea, ca. 2 km^3 per year. This allowed the surface brine level to partially recover. In 1992 the dam between the Kara-Bogaz-Gol Gulf and the Caspian Sea was completely demolished. After the destruction of the dam, the volume of seawater entering from the sea to the Gulf was determined by the difference between the levels of the sea and the gulf. This difference decreased from 6.50 m in 1991 to ca. 0.49 m in 1996 and remained constant for the next six years (Fig. 1). The formation of new surface brines started being conditioned by both the evaporation of entering seawater and the interaction of seawater and brines with salt deposits formed during the Gulf evaporation. At first, the volume of seawater entering Kara-Bogaz-Gol Gulf was about 50 km^3 per year. However, during the last years this volume dropped to about 20 km^3 per year. The Gulf reached its natural dimensions at present shorelines. The volume of the surface brines is 25-30 $км^3$, the Gulf water area is ca. 20,000 km^2 and its maximum depth is about 8-10 m. The natural variation of the Caspian Sea level, until the mid eighties, was discussed by Akovetskii and Bogdanov (1988).

Fluctuations of the water level changes at the Kara-Bogaz-Gol are determined mostly by annual water influx from the Caspian Sea and by water evaporation from the Gulf surface. At present, there seem to be a stabilization of seawater influx (18-19 km^3/year), however, the volume of influx seawater is slightly less than that of water evaporation from the gulf surface (Table 1). As a result of the negative water balance, increased mineralization of Gulf brines was noted.

The surface brines reached sodium sulfate saturation and during the last years mirabilite crystallization was observed in the Gulf. Over the last several years, the chemical analysis of surface brines for the content of major ions (Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^-, SO_4^{2-}, HCO_3^-) and minor ions (B_2O_3, Br^-, Li^+, heavy metals) demonstrated that the chemical composition of brines began to be stable with mineralization reaches 29-31%. The concentrations of the industrially important components (sulfate, potassium, bromide and boron ions and microelements) increase averagely by 5 % per year and reached the following values: 2.72-2.88% SO_4^{-2}, 0.11-0.12% K^+, 150 mg/l Br^-, 130 mg/l H_3BO_3, 5-6 mg/l Li^+. The current brines, as compares to the brines prior to the construction of the dam are depleted of sulfate and potassium ions but richer in boron, bromine and rare metals. The composition of the surface brine in wintertime is located on the solubility diagram of the system Na^+, Mg^{2+}, Cl^-, SO_4^{2} - H_2O at 0°C in the field of Na_2SO_4 crystallization. The Kara-Bogaz-Gol Gulf has returned to be a unique basin for industrial mineral precipitation.

The surface brines were used for industrial scale production of sodium sulfate in 1934-1956. At present time, industry uses underground and buried brines of the second level of Kara-Bogaz-Gol Gulf for production of glauberite ($Na_2SO_4 \cdot 10H_2O$), bischofite

($MgCl_2 \cdot 6H_2O$), epsomite ($MgSO_4 \cdot 7H_2O$) and other minerals. These brines at density of 1.23-1.24 g·cm^3 contain more than 7.7% sodium sulfate and less than 8.5% magnesium chloride. The technological process of mirabilite production will be discussed later. The most promising raw materials are the surface brines, since they are renewable, inexhaustible ((1-2)·10^{12} kg of mineral salts reach the Kara-Bogaz-Gol Gulf with seawater each year) and are at the Gulf surface. These factors determine the minimum expenses for transport and production.

III. SCIENTIFIC SUMMARY & EXPERIMENTAL PART

1. Sampling places

The best place for sampling surface brine was at the northwest shore in the vicinity of the existing mineral production plant. The sampling was done in an area ca. 500 m from a dam, between Karasukut Bay, the central zone and a canal, which connected Karasukut Bay and the central zone (Fig. 2). It was found that mineralization of Kara-Bogaz-Gol brines in various parts of the lagoon appeared to be different. The mixing zone, where the water of the Caspian Sea flows into the gulf, had variable composition and the lowest salt concentrations. The highest mineralization was observed in the central zone and in the northwest coastal zone. The coordinates of sampling stations in these zones, which have been used since are presented in Table 2. Statistical analysis of the chemical composition of Kara-Bogaz-Gol water since 1995 has shown that the composition of brines in the central zone, in Sartas Bay and ca. 500 m from a dam between Karasukut Bay and the central zone are almost identical. At these stations, at the same sampling period, the difference between concentrations of particular ions and total salts content is less than 5%. The data for comparison is presented in Table 3. All the above mentioned allowed us to assume that composition of brine sampled 500 m from a dam between Karasukut Bay and the central zone is average for northwest shore zone.

2. The composition of Kara-Bogaz-Gol surface brines

Brine samples were kept in glass bottles with ground glass stoppers. Contents of major ions in the brines were determined using the following standard techniques:

Ionic concentration	Method of determination
Cl^-	Volumetric argentometric titration
SO_4^{2-}	Gravimetric analysis in the form of $BaSO_4$
CO_3^{2-} and HCO_3	Volumetric titration using 0.05M HCl, phenolphtalein and methilorange as indicators.
Ca^{2+} and Mg^{2-}	Complexometric analysis (0.001N solution of trilon was used for titration by using an automatic METTLER TOLEDO DL50 Titrator).
K^+ and Na^+	Flame photometry method using Flame Photometer 410.
Boron	Volumetric titration using 0.01 M NaOH with mannit for complexation and with methyl-rot and phenol-rot as indicators.
Br^-	Ion selective electrode DX280-Br^- and METTLER TOLEDO DL50 Titrator.

The standard solutions were prepared by using solutions resembling the surface brines. The natural solutions and solid phases, formed in the evaporation process, were either diluted

or dissolved in distilled water. The relative precision of the Cl^-, SO_4^{2-}, HCO_3^-, Ca^{2+}, Mg^{2+}, K^+ and Na^+ determination was as follows: 0.10%, 0.05%, 0.20%, 0.20%, 0.05%, 1.19%, 0.45%, respectively.

The physical properties and composition of the Kara-Bogaz-Gol surface brines and sediments are presented in Table 3. The obtained data indicated that the concentration of salts increases during the summer. The largest mineralization (26.12%) was observed in August. In November, when temperature of the brine reached less than 10°C, precipitation of mirabilite occurred. At present, the shore zone is covered by a layer of mirabilite containing small quantities of halite and epsomite (Table 3). Due to a combination of favorable conditions, the Gulf represents a natural pool for precipitation of mirabilite ($Na_2SO_4 \cdot 10H_2O$). The brine for investigating the mirabilite precipitation and solar evaporation was sampled at Station #2. Existing observations for seasonal changes of chemical brine composition demonstrated that maximum mineralization was reached in September-October before the rainy season. The brines were found to be formed only due to seawater influx of and water evaporation from the Gulf surface. It is possible that the dissolution of bottom minerals settled during the phenomenon of gulf dry-up when the gulf was separated from the Caspian Sea by a dam is completely accomplished. The analysis of the data obtained allows us to conclude that the depth of surface brines mixing does not exceed 3 m. At present, there are no conditions for massive mineral precipitation from Kara-Bogaz-Gol waters. Only the precipitation of mirabilite during winter months (January-February) was observed.

The composition of Kara-Bogaz-Gol buried brines from two production wells used at the present for the production of mirabilite, epsomite and bischofite are also presented in Table 3. The composition of the surface brines and the buried ones are almost identical. The only difference we found is that buried brines are relatively richer in magnesium and sulfate ions and in content of H_2S (150-280 mg/l).

The composition of the Kara-Bogaz-Gol surface brines is presented in Table 4. The comparison of brine compositions, sampled in 2002 and in 2003, at the same season demonstrates the stability of the surface brine. In November 2002 and 2003, when temperature of the brine reached less than 10°C, precipitation of mirabilite ($Na_2SO_4 \cdot 10H_2O$) occurred. The precipitation of other minerals was not observed.

3. Drainage of Caspian Sea water to Kara-Bogaz-Gol

The data related to the drainage of Caspian Sea water into Kara-Bogaz-Gol (Table 5) shows that that after the stabilization of the drainage on the level 18-19 km^3/year during 1997-2001 the drainage began to decrease during 2002 and 2003. This phenomenon is very important for the formation of the surface brines of Kara-Bogaz-Gol.

4. Solar evaporation of the Kara-Bogaz-Gol surface brine

The main process of brine preparation for industry takes place in ponds. This method allows using the advantage of the arid climate of Turkmenistan: high summer temperature, low air humidity, more than 300 sunny days per year. The solar evaporation of Kara-Bogaz-Gol surface brines was studied in two ways:

a) thermodynamic modeling of water evaporation developed by Prof. Boris Krumgalz;
b) experimental brine evaporation in laboratory conditions.

The experiments and modeling calculations of the sampled brines were carried out on the sample taken on 13.06.2003 at #2 sampling station with coordinates N41°37', E52°44' (Karasukut dam - a zone of the Gulf close to the plant).

5. Experiment on solar evaporation of surface brine

Surface brine is the raw material for production of mineral salts. Therefore, preparation of surface brine in the pond method is the basis for future technology. The study of solar evaporation of surface brine was done to determine the conditions under which the existing technology for processing the buried brines can be used for processing surface brines. The purpose of our experiment was to determine the sequence of mineral crystallization and the distribution of major brine components between liquid and solid phases during the process of solar evaporation that depend on initial brine composition.

The study of solar brine evaporation was carried out in laboratory conditions by the method developed in the Turkmenistan Institute of Chemistry (Khodjamamedov et al., 1991; Davletova et al, 1988). The method developed was very similar to natural conditions. A shallow glass vessel was filled with brine and left outdoors exposed to wind and sun. The temperature was measured every day at 10 A.M. and at 4 P.M. The mean values of air and brine temperature were 32°C in the morning and 37°C in the afternoon (Table 6). The initial brine volume was 10.0 dm^3. The separation of liquid and solids was done by vacuum filtration when approximately 10% of the water was evaporated or if new solid crystals were formed. The weights of liquid and solids were measured with an accuracy of ±10 g (at the beginning of the process) and ±0.03 g (when the brine reached 1.0 dm^3). The process lasted from 9.07.2003 to 25.08.2003, when the eutectic point was reached.

6. Results and discussion

The compositions of liquids and solids formed during solar evaporation of surface brine, sampled at 13.06.2003 are presented in Table 7. After separation of liquids and solids, at each step of evaporation, only liquids were conditioned for further evaporation. The compositions of solids are compositions of new precipitates.

The gypsum mineral is the first to crystallize and cover the surface of brine as thin film. Then starts the crystallization of halite. The joint precipitation of gypsum and halite occurs at ionic strength between 8.72 and 9.98. It should be noted that halite precipitates during the entire evaporation process and its crystals are present in all solids. Starting from the ionic strength 9.98 the precipitation of bloedite takes place. The mixture of bloedite and halite crystallizes until reaching the ionic strength 12.67. Then joint precipitations of epsomite and halite are observed. The further brine evaporation to the ionic strength larger than 18.0 leads to precipitation of complex potassium and magnesium minerals (carnallite, hexahydrite, and kainite). The bischofite crystallization starts at ionic strength higher than 18.36.

Crystal formation was determined by chemical analysis of the solids and suggested by graphic calculation using Schrainemaker's method for solubility diagrams of aqueous salt systems, microscope and X-ray investigations. The photos of solids sampled at various stages of brines evaporation demonstrated the following minerals:

Photo #	Mineral	Mineral description
S-1	Halite	Regular cubic form
S-2	Astrahanite = Bloedite	Pentahedron
S-3	Epsomite	Large wedge-shaped crystals
S-4	Carnallite + Kainite	
S-5	Bischofite	Acicular (needle) crystals

Photos of minerals precipitated at various stages of brines evaporation

$5

The X-ray spectrum of solid phases demonstrated that the halite precipitated at all precipitation phases. The spectrum allowed determination of bloedite (spectrum of phases #2-4), gypsum (spectrum of phases #4), hexahydrite (spectrum of phases #3-6), kainite (spectrum of phases #6) and bischofite (spectrum of phases #7). Thus, we received under the experimental study of solar evaporation of the Kara-Bogaz-Gol Gulf brine the following sequence of minerals precipitation: gypsum, halite, bloedite, hexahydrite, epsomite, kainite, carnallite, and bischofite.

The obtained results will be basis for the development of the technology for the production of various minerals from surface Kara-Bogaz-Gol brines. It should be emphasized here that we succeeded to receive brine with the content of potassium ions equal to 1.26% wt. (liquid phase #5), which is very promising for the production of mixed potassium fertilizes.

7. The development of the dynamic model for natural water evaporation

The application of physico-chemical modeling for understanding the evolution of natural water bodies is very useful. Since the early work of Van't Hoff, geochemists have compared, as common practice, the results of natural water analysis with computed saturation levels in order to obtain information about mineral precipitation and dissolution in natural brines. This approach provided the basis for interpreting field data in terms of the chemical behavior, which influenced the formation of evaporative sediments (Garrels and Thompson, 1962; Helgeson, 1969). The semi-empirical approach developed by Pitzer and his school (Pitzer, 1973, 1979, 1991 and references therein) allowed the estimation of salt saturation conditions in very concentrated electrolyte solutions, including various hypersaline brines. The composition of most natural brines includes the major ions Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cl^-, Br^-, HCO_3^-, CO_3^{2-} and SO_4^{2-}. Such chemical composition describes seawater-derived brines, waters associated with continental evaporites, formation brines of mixed origin, deep-sea hydrothermal vents, etc. The approach developed by Pitzer's scientific school, though semi-empirical in character, has been quite successful in predicting the thermodynamic properties of mixed electrolyte solutions over a wide range of solution concentrations. This approach is based on a set of theoretically and empirical-derived equations that account for the interactions between the particular ions present in a solution and for indirect forces arising from the ion-solvent interactions. Predicting various thermodynamic properties of multiple-electrolyte solutions by Pitzer's approach was based on the use of so-called ion interaction parameters, calculated from the appropriate experimental data for single and ternary electrolyte solutions. This model avoided some of the restrictions or assumptions required by previous models, such as the intrinsic limitation to low or moderate concentrations or the extrapolation of some of the solution properties beyond the solubility limit of electrolytes in pure water. The Pitzer approach proved to be especially effective for predicting various thermodynamic properties of natural hypersaline brines of large complexity. Harvie and Weare (1980) and Harvie et al. (1980, 1982, 1984) were the first who successfully applied the Pitzer ion interaction approach to the geochemical development of natural brines. This was done by calculating the variation of seawater composition and mineral precipitation during isothermal evaporation. During recent years, Krumgalz has intensively applied Pitzer's approach to geochemical studies in, both, Dead Sea waters and in its various mixtures with Mediterranean Sea water (Krumgalz and Millero, 1982, 1983, 1989; Krumgalz, 1996, 1997, 2001).

The dissolution-precipitation equilibrium of an ionic mineral of a formula $M_{\nu_M}X_{\nu_X} \cdot nH_2O$ can be described as:

$$M_{\nu_M}X_{\nu_X}\cdot nH_2O \xleftrightarrow{K_{sp,M_{\nu_M}X_{\nu_X}\cdot nH_2O}} \nu_M\cdot M^{+z_M}+\nu_X\cdot X^{-z_X}+n\cdot H_2O \quad (1)$$

where ν_M, ν_X, z_M and z_X are the ionic amounts in a mineral molecule and the charges of cations (M) and anions (X), respectively, n is the number of water molecules in a mineral molecule, and $K_{sp,M_{\nu_M}X_{\nu_X}\cdot nH_2O}$ is the thermodynamic equilibrium constant of the dissolution-precipitation equilibrium of this ionic mineral. A thermodynamic equilibrium constant can be calculated if the standard state chemical potentials of the solid and aqueous species are available at the temperature and pressure of interest. The equilibrium constant for the above dissolution-precipitation process is expressed as:

$$\ln K_{sp,M_{\nu_M}X_{\nu_X}\cdot nH_2O} = \frac{\mu_S^o-(\nu_M\cdot\mu_M^o+\nu_X\cdot\mu_X^o+n\cdot\mu_{H_2O}^o)}{R\cdot T} \quad (2)$$

where μ_S^o, μ_M^o, μ_X^o and $\mu_{H_2O}^o$ are the standard chemical potentials of a mineral (in solid state), of a cation and anion in solution, and of water, respectively, R is the gas constant, and T is the temperature in Kelvin degrees. If the activity of the solid phase is considered to be equal to 1, then this constant is defined as:

$$K_{sp,M_{\nu_M}X_{\nu_X}\cdot nH_2O} = a_{M,sat}^{\nu_M}\cdot a_{X,sat}^{\nu_X}\cdot a_{H_2O}^n = (m_{M,sat}\cdot\gamma_M)^{\nu_M}\cdot(m_{X,sat}\cdot\gamma_X)^{\nu_X}\cdot a_{H_2O}^n \quad (3)$$

where $a_{M,sat}$, $a_{X,sat}$, $m_{M,sat}$ and $m_{X,sat}$ are the activities and molal concentrations of cation and anion, respectively, in the liquid phase saturated with respect to the solid phase, γ_M and γ_X are the conventional single-ion activity coefficients of cation and anion at a proper concentration, respectively, and a_{H_2O} is the water activity of the liquid phase, defined as:

$$a_{H_2O} = \frac{p}{p_o} = \exp\left(-\frac{\phi}{55.51}\cdot\sum_i m_i\right) \quad (4)$$

where p and p_o are the saturated vapor pressure of solution and pure solvent at the same temperature, respectively, ϕ is the osmotic coefficient of a particular solution, and $\sum_i m_i$ is the summation of molalities of all solute species, including ionic species and neutral substances in the solution. The standard chemical potential of water and the water activity should not be included in Eqns. 2 and 3, respectively, if a mineral molecule does not contain water molecules.

In general, the degree of saturation (Ω) of minerals of the formulas either $M_{\nu_M}X_{\nu_X}$ or $M_{\nu_M}X_{\nu_X}\cdot nH_2O$ is defined by the following equations:

$$\Omega_{M_{\nu_M}X_{\nu_X}} = \frac{m_{M,i}^{\nu_M}\cdot m_{X,i}^{\nu_X}}{m_{M,sat}^{\nu_M}\cdot m_{X,sat}^{\nu_X}} = \frac{m_{M,i}^{\nu_M}\cdot m_{X,i}^{\nu_X}}{K_{sp,M_{\nu_M}X_{\nu_X}}\Big/\left(\gamma_{M,sat}^{\nu_M}\cdot\gamma_{X,sat}^{\nu_X}\right)} \quad (5)$$

$$\Omega_{M_{\nu_M}X_{\nu_X}\cdot nH_2O} = \frac{m_{M,i}^{\nu_M}\cdot m_{X,i}^{\nu_X}}{m_{M,sat}^{\nu_M}\cdot m_{X,sat}^{\nu_X}} = \frac{m_{M,i}^{\nu_M}\cdot m_{X,i}^{\nu_X}}{K_{sp,M_{\nu_M}X_{\nu_X}\cdot nH_2O} \Big/ \left(\gamma_{M,sat}^{\nu_M}\cdot\gamma_{X,sat}^{\nu_X}\right)\cdot a_{H_2O}^{n}} \tag{6}$$

where the $m_{M,i}$ and $m_{X,i}$ are the molal concentrations of cation and anion in a particular system, respectively. The most modern and complete Pitzer's equations for conventional single ion activity coefficients and water activity are:

$$\begin{aligned}\ln\gamma_M = {} & z_M^2 f^\gamma + 2\sum_a m_a(B_{M,a} + EC_{M,a}) + z_M^2\sum_c\sum_a m_c m_a B_{c,a}^\phi + z_M\sum_c\sum_a m_c m_a C_{c,a} + \\ & \sum_c m_c(2\Theta_{M,c} + \sum_a m_a\Psi_{M,c,a}) + \sum_a\sum_{<a'} m_a m_{a'}\Psi_{a,a',M} + \\ & 2\sum_c m_c\,{}^E\Theta_{M,c} + z_M^2(\sum_c\sum_{<c'} m_c m_{c'}\,{}^E\Theta'_{c,c'}) + z_M^2(\sum_a\sum_{<a'} m_a m_{a'}\,{}^E\Theta'_{a,a'})\end{aligned} \tag{7}$$

$$\begin{aligned}\ln\gamma_X = {} & z_X^2 f^\gamma + 2\sum_c m_c(B_{c,X} + EC_{c,X}) + z_X^2\sum_c\sum_a m_c m_a B_{c,a}^\phi + |z_X|\sum_c\sum_a m_c m_a C_{c,a} + \\ & \sum_a m_a(2\Theta_{X,a} + \sum_c m_c\Psi_{X,a,c}) + \sum_c\sum_{<c'} m_c m_{c'}\Psi_{c,c',X} + \\ & 2\sum_a m_a\,{}^E\Theta_{X,a} + z_X^2(\sum_c\sum_{<c'} m_c m_{c'}\,{}^E\Theta'_{c,c'}) + z_X^2(\sum_a\sum_{<a'} m_a m_{a'}\,{}^E\Theta'_{a,a'})\end{aligned} \tag{8}$$

$$\begin{aligned}a_{H_2O} = \exp\Bigg\{ & -\frac{\sum_i m_i}{55.51}\cdot\Bigg[1 + 2(\sum_i m_i)^{-1}[-\frac{A^\phi I^{3/2}}{1+bI^{1/2}} + \sum_c\sum_a m_c m_a(B_{c,a}^\phi + \\ & \frac{E}{|z_c z_a|^{1/2}}C_{c,a}^\phi) + \sum_c\sum_{<c'} m_c m_{c'}(\Phi_{c,c'}^\phi + \sum_a m_a\Psi_{c,c',a}) + \\ & \sum_a\sum_{<a'} m_a m_{a'}(\Phi_{a,a'}^\phi + \sum_c m_c\Psi_{a,a',c}) + \sum_n\sum_a m_n m_a\lambda_{n,a} + \sum_n\sum_c m_n m_c\lambda_{n,c} + \\ & \sum_n\sum_{<n'} m_n m_{n'}\lambda_{n,n'} + \frac{1}{2}\sum_n m_n^2\cdot\lambda_{n,n}]\Bigg]\Bigg\}\end{aligned} \tag{9}$$

The detailed information regarding the meanings and calculations of all parameters in Eqns. 7-9 can be found in Krumgalz and Millero (1982, 1983), Harvie et al. (1984), Pitzer (1991). Eqns. 7-9 take into consideration various interactions of opposite-charged ions, like-charged ions, triple ionic interactions, and asymmetrical electrostatic mixing effects. Throughout this equation, the subscripts "M" and "c" refer to cations, while the subscripts "X" and "a" refer to anions. The values m_c and m_a are the molal concentrations of a proper cation and anion, respectively, while the symbols $\sum_a$, $\sum_c$ and $\sum_n$ indicate the summation of the properties respectively to all anions, all cations and all neutral species, respectively. The double summation indices, $\sum_c\sum_{<c'}$, $\sum_a\sum_{<a'}$, $\sum_n\sum_c$, $\sum_n\sum_a$ and $\sum_n\sum_{<n'}$, denote the

proper sum over all possible pairs of variations of all cations, anions or their pairs with neutral species, respectively.

8. Thermodynamic model for water evaporation and mineral precipitation from natural brines.

A short description of the developed thermodynamic model for water evaporation and mineral precipitation from natural brines is given below. The input data for the model includes ionic concentrations (in molal units), thermodynamic products of mineral solubility and Pitzer's ion interaction parameters. Sometimes, the values of the thermodynamic products of mineral solubility and the Pitzer ion interaction parameters in literature differ considerably (Pitzer, 1979, 1991; Kim & Frederick, 1988a,b and Marshall et al., 1995). Therefore, the selection of the thermodynamic products of mineral solubility and the ion interaction parameters for the calculations in multiple component systems should be carried out very cautiously. Table 1A (in Appendix) contains the most reliable thermodynamic solubility products at 25°C of all possible minerals formed from various combinations of major ions of natural waters: Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cl^-, Br^-, HCO_3^-, CO_3^{2-} and SO_4^{2-}, reviewed from the existing literature data. The latest extended review of the ion interaction parameters was presented by Pitzer (1991), while some additions and revisions of those for major ions have been recently proposed by Krumgalz (1997). Tables 2A and 3A (in Appendix) summarize the Pitzer ion interaction parameters for all possible ion combinations for major ions of natural waters. The products of solubility and Pitzer's ion interaction parameters from Tables 1A-3A were used for developing a database. This database was then embedded in the simulation program with an interface that enabled the external correction of data. In the final form of our program, the temperature dependencies of the parameters in Tables 1A-3A were also taken into account.

Although mineral precipitation from natural waters under isothermal evaporation is controlled by kinetic and by thermodynamic factors, only the latter were taken into consideration and each mineral with $\Omega_i>1$ is considered to precipitate until its degree of saturation reaches the value $\Omega_i \leq 1.0000 \pm 0.0001$. At each stage of precipitation, a mineral with the largest Ω_i will precipitate. At the initial step, the model calculates single-ion activity coefficients, water activity of the brine at a proper temperature and the degrees of saturation of all possible minerals. Three possible cases are discussed below:

a) If the initial brine is undersaturated with respect to all minerals, and their degrees of saturation (Ω_i) in the system are less than 1.0, then, the water evaporation may be simulated by removing H_2O from the brine by iteration in several steps. The changes in ionic concentrations and the degrees of mineral saturation are calculated at each step of the water removal. If during water removal the solution becomes oversaturated, the model retreats one-step and then subtracts smaller amounts of water, until the saturation with respect to any possible mineral is reached ($\Omega_i=1.0000 \pm 0.0001$).

b) If the initial brine is oversaturated with respect to any mineral ($\Omega_i>1.0001$), another subroutine simulates the process of mineral precipitation from this brine up to its saturation state. When more than one mineral has values of $\Omega_i>1.0001$, precipitation takes place according to the Ω_i's values, starting with the highest. During precipitation, Ω values change and the supersaturated minerals may precipitate intermittently simulating a mineral "simultaneous" sedimentation. At this stage, the precipitation of the mineral is expressed by subtracting a certain portion (for instance 10%) of the smallest concentration amongst the ions forming this particular mineral. If the amount of the precipitated mineral is too large and the obtained solution becomes undersaturated with respect to this mineral, the model retreats one step. Then, by

subtracting half of the initial portion of the mineral, the calculation procedure is repeated until saturation (with respect to this mineral) is reached (Ω_i=1.0000±0.0001). The process is repeated for all other minerals with Ω_i>1, as well.

c) The solution is saturated with respect to at least one single mineral (Ω_i=1.0000±0.0001). This case includes the final stages of cases "a" and "b" as well. A subroutine simulates the process of water evaporation from such saturated brine. The user determines the amount of evaporated water and the obtained oversaturated brine is treated as in case "b".

The reconstruction of the evolution history of natural brines subjected to evaporation requires knowledge of the concentration changes of one or more conservative constituents. Such a conservative constituent must never precipitate during the evaporation of a natural brine, nor participate in diagenic reactions with mineralogical environment. Considering the composition of various highly saline natural brines, it is possible to conclude that only bromide (amongst major ions) meets the above requirements. Thus, the "inert" character of the bromide during the evaporation of natural waters makes it ideal for tracing the chemical evolution of natural brines subjected to evaporation. Earlier, Rittenhouse (1967) used the changes in bromide concentration for to determine the origin of some oil-field brines. The degree of brine evaporation can be characterized by an enrichment factor, f_{enrich}, defined as

$$f_{enrich} = \frac{G_{H_2O}}{G_{H_2O} - \left(g_{H_2O}\right)_{removed}} \tag{10}$$

or

$$f_{enrich} = \frac{[\text{conservative ion}]_i}{[\text{conservative ion}]_{initial}} \tag{11}$$

where G_{H_2O} and $\left(g_{H_2O}\right)_{removed}$ are the weights of water in the initial brine at the beginning of the evaporation process, and the weight of water removed from the brine at each stage by water evaporation and/or precipitation of a hydrated mineral, respectively; [conservative ion]$_i$ and [conservative ion]$_{initial}$ are the concentrations of a conservative ion at a given degree of brine evaporation and in initial brine, respectively. As we mentioned above, the Br^- ion would be further considered as a conservative ion for natural brine evaporation, since no bromide containing minerals precipitate in the lake during its evaporation and no bromide participation in diagenic reactions with mineralogical environment is known. Removal of water from brine is governed by evaporation and, to a lesser amount, by the precipitation of hydrated minerals such as $KMgCl_3 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, $Mg_2CaCl_6 \cdot 12H_2O$, $CaCl_2 \cdot 4H_2O$, etc.

9. Results of thermodynamic modeling for water evaporation and mineral precipitation from Kara-Bogaz-Gol brine

The process of solar evaporation of surface brine from KBG Gulf was modeled using the thermodynamic model for water evaporation and mineral precipitation from natural brines developed by Prof. Krumgalz. The calculations were done at 30°C, nearly average for a day during solar evaporation. The obtained results were compared with the experimental data. The compositions of liquid and solid phases formed during experimental solar evaporation of surface brine are presented in Table 7, while the compositions of liquid phase determined by model calculations are presented in Table 8. It must be noted that the major ionic concentrations determined experimentally and by calculation are in good agreement at approximately identical ionic strengths (Fig. 3) except for potassium ions (Fig. 4).

The composition of the solids formed during solar evaporation are presented in Table 9 while the mineralogical compositions of solids obtained under model calculation of solar evaporation are presented in Table 10. In general, there is good concurrence between experimental and calculated data. However, it should be noted that there are some differences. For instance, at the beginning the precipitation of calcium sulfates and carbonates occur as shown by model calculations. However, the used experimental technique could not detect these minerals due to their small trace amounts. To explain this, it should be noted that the model calculations reflects ideal thermodynamic situation that does not exist in nature. In natural conditions, the influence of kinetic factors and the formation of the oversaturated solutions can explain either the delayed precipitation of some minerals or their absence. It is known that the amount of water molecules combined with magnesium sulfate under natural waters evaporation depends on the condition of the evaporation: temperature, humidity, wind. Therefore, the differences in the water content in magnesium sulfate minerals obtained in experimental evaporation and in model evaporation in isothermal conditions are natural. Thus, it was demonstrated that the developed model of the evaporation of natural waters could be successfully applied to solar evaporation of surface brines of Kara-Bogaz-Gol Gulf.

IV. DEVELOPMENT OF A TECHNOLOGY SCHEME FOR COMPLEX PROCESSING OF SURFACE BITTERNS OF KARA-BOGAZ-GOL GULF

Based on the above, the experimental results and model calculations of the composition of liquid and solid phases formed in the process of solar evaporation of the surface brines of Kara-Bogaz-Gol Gulf, we chose the degrees of solution evaporation which allow organizing the production of halite, epsomite, potassium salts and chlorate-magnesium defoliant. Below are two suggested variants for the complex production of surface gulf brines.

1. First variant

This variant consists of the following sequence of salt extraction from evaporation basin: halite – sodium sulfate – epsomite – potassium minerals – bischofite (Fig. 5a). Brine from the Gulf is pumped into a storage pond (I) where the preliminary brine concentrating takes place until the starting of halite precipitation (at ionic strength equal to 8.74). Then liquid phase gravity flows to the second pond (II). In this pond the precipitation of the major quantity of very clear halite occurs. After the halite precipitation and when the solution density reaches 1.252 g/l the brine is pumped into the pond (III). In this pond further precipitation of the halite takes place with simultaneous concentrating of sodium and magnesium sulfates. In order to exclude the precipitation of sulfate containing minerals, small quantity of seawater is supplied to this pond. Then, the concentrated brine is pumped into the fourth pond (IV) where after reaching sulfate concentration of 7.5-8.0%, the following minerals precipitate: bloedite (astrakanite) and halite. The precipitate obtained in this pond contains about 60% sulfate salts (sodium and magnesium) and about 40% of halite. According to this variant of complex processing the precipitate obtained in the fourth pond is dissolved in seawater and is cooled to 0°C. At these conditions $Na_2SO_4 \cdot 10H_2O$ is precipitated from the cooled brine. $Na_2SO_4 \cdot 10H_2O$ production can be conducted either by industrial method (artificial cooling) or by pond method (natural cooling during winter). The formed brine is pumped in the fifth pond (V) called epsomite basin. In this pond the precipitation of epsomite occurs and the brine is enriched in potassium and magnesium. The epsomite mother

brine with potassium chloride concentration 2.3-2.4% is transferred to the sixth evaporating basin (VI) where the precipitation of so-called raw potassium salt takes place. The raw potassium salt in layers is washed by rain and is drained from the mother brine. Then the salt is collected in clamps, dried by wind and sun, and used in the production of chloride free potassium fertilizer as raw material. Then the mother brine with high content of magnesium chloride (till 29-31%) is transferred to the seventh pond (VII), which serves as storage for potassium, sodium and sulfate ions. After the seventh pond, the brine is transferred to the plant for bischofite production, which, in turn, is raw material for the production of magnesium chloride defoliant.

2. Second variant

This variant consists of the following sequence of salt extraction from evaporation basin: mirabilite (either by industrial method or by pond one), halite – epsomite – potassium minerals – bischofite. At industrial method of mirabilite extraction the temperature of surface brines decreases at 0°C in special tanks where the precipitation of mirabilite takes place. The mother brine moves into storage tank for concentrating and halite precipitation. The further technological steps are identical with the first variant of brine processing. In the case of the sodium sulfate production by the pond method the surface brine is pumped in the first pond and concentrated preliminarily (Fig. 5b). In order to avoid the sulfate precipitation together with halite the brine is diluted, if necessary, with seawater. During the winter, when the brine temperature reaches +5°C÷0°C, the mirabilite precipitation begins. The mother brine after the mirabilite extraction is moved into evaporation ponds. Then all further processes and the sequence of minerals extraction are the identical to the first variant of brine processing.

3. Crystallization of mirabilite and the evaporation of mirabilite mother brine

It is known that two sorts of solutions containing sulfate ions are the most practical. Solutions from which either mirabilite or epsomite crystallize under cooling (Lepeshkov, Bujnevich and Sedelnikov, 1981). Since the Kara-Bogaz-Gol brines are considered as the unique raw material for mirabilite production, we have been investigating the possibility of producing pure mirabilite from surface brine. The figurative brine composition point on the solubility diagram of aqueous salt system $2Na^+$, $Mg^{2+}/2Cl^-$, SO_4^{2-} - H_2O at 0°C is situated in the field of mirabilite crystallization, but at 25°C figurative brine composition point is situated in the field of halite crystallization and NaCl concentration is high. We suggested that mirabilite could precipitate together with halite. Such a precipitation is a negative technological factor.

Mirabilite was precipitated by slow decrease of brine temperature to 0°C in permanent mixing. This imitates industrial production of mirabilite. Mirabilite was crystallized without any addition of seed crystal. The obtained pulp was separated with Büchner funnel by using a vacuum pump. The preliminary study of the process of mirabilite crystallization was carried out for 2 brines: surface brine and an evaporated surface brine (about 10% of brine's water was evaporated). The second brine was used because the salt concentration in surfaces brine has increased every year and we would like to know the composition of mirabilite produced in the future. The composition of initial brines and sediments are presented in Table 11.

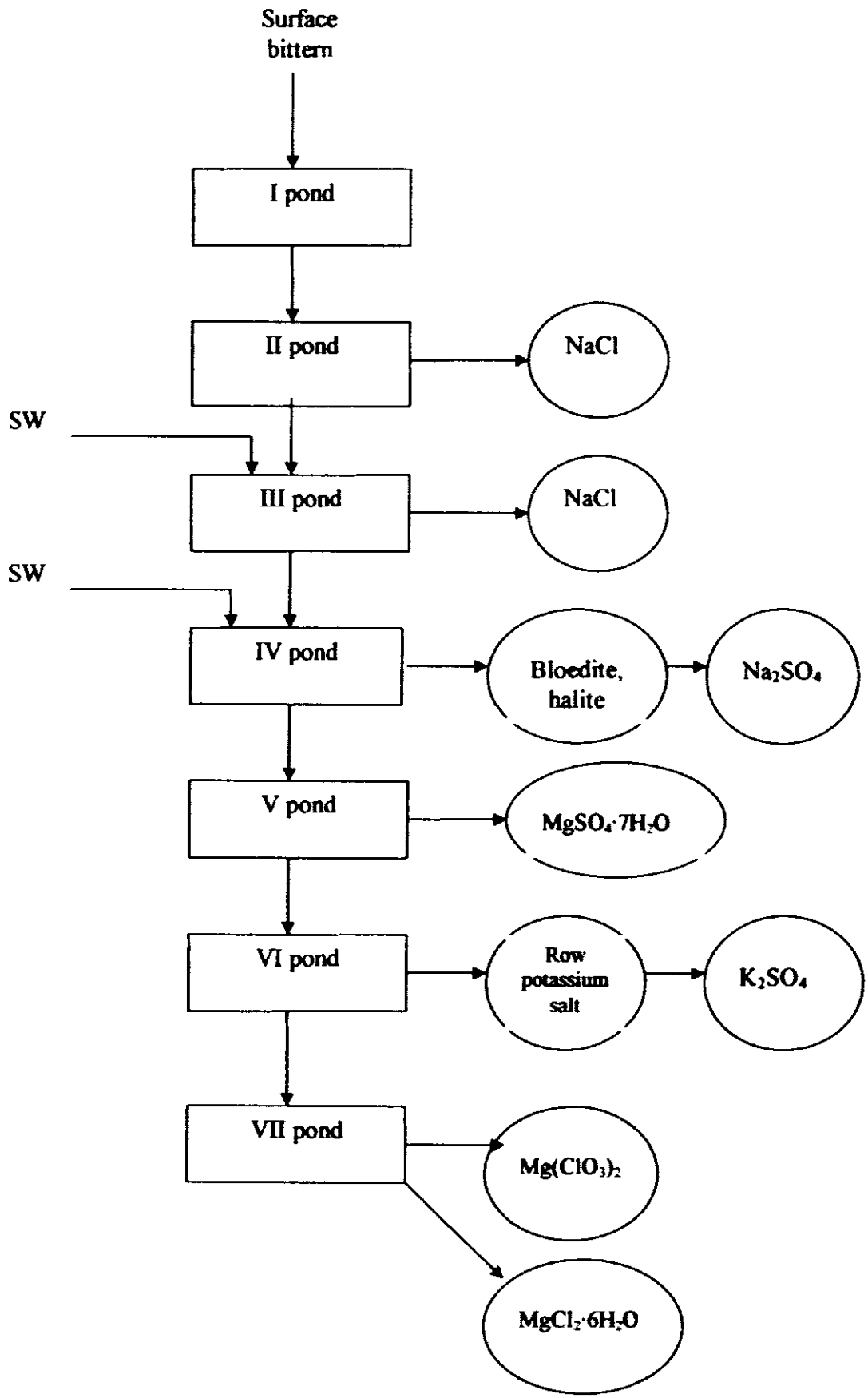

Fig. 5a. Principal process flow sheet of Kara-Bogaz-Gol surface brine complex technology (variant #1)

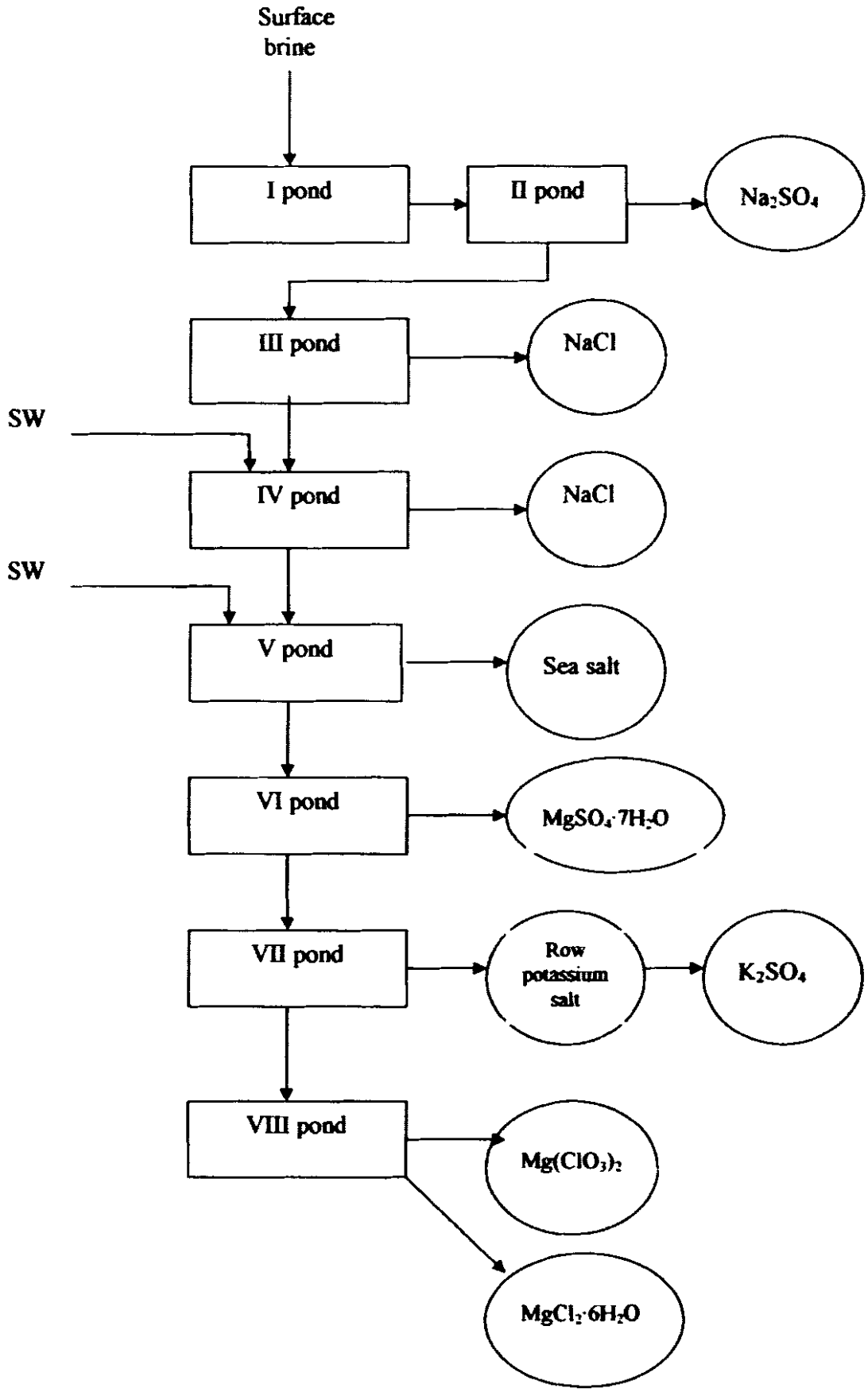

Fig. 5B. Principal process flow sheet of Kara-Bogaz-Gol surface brine complex technology (variant #2)

From the present surface brine the almost pure mirabilite suitable for the production of medical Glauber's salt was obtained. The quality of the precipitated mirabilite has begun to be poor as surface brine increases. Mirabilite precipitated from the evaporated surface brine includes up to 5% of NaCl. However, even from such mirabilite the medical Glauber's salt can be obtained by washing out the NaCl inclusions. The yields of mirabilite from surface brine and from the evaporated brine are 119 and 142 kg/m^3, respectively. These numbers are comparable with mirabilite yield from buried industrial brines. Therefore, in the near future the most perspective technology will be the technology based on the mirabilite crystallization. This technology will use either pond method in wintertime or industrial cooling. Lepeshkov and others (1981), Bujnevich and others (1992), Atadjanov and Kurilenko (1991) showed that the mirabilite yield increases until the astrakanite precipitation starts. Thus, according to the results of model evaporation of surface brine, the technology based on mirabilite crystallization can be applied until it reaches solution ionic strength of about 9.5.

We studied also the possibility to utilize the mirabilite mother brine in the pond method. The experimental procedure was identical to those used for the solar evaporation of surface brine. The compositions of liquid and solid phases obtained during the solar evaporation experiments are summarized in Tables 12 & 13. In the evaporation process in the ionic range 6.5-13.4 only the precipitation of halite was observed. Then, the precipitation of minerals with high content of magnesium and sodium sulfates started. In ionic strength large than 15.3, the mixture of salts with high content of potassium was formed. It should be noted that, in solar evaporation, salt mixture containing more than 40% potassium salts and about 30% crystalline hydrates of magnesium sulfate formed in both surface brine and mirabilite mother brine. This shows that potassium fertilizers can be produced from these two raw materials. In view of the above results, we suggest complex processing of surface brines based on mirabilite crystallization with further evaporation of mirabilite mother brine in pond system (Fig. 5b). In contrast to the first variant, brine from the storage pond (I) is moved for sodium sulfate extraction, which can be done either by the industrial or by the pond method. The formed mirabilite mother brine is then processed as in the first variant.

4. Development of technology for production of potassium sulfate from surface bitterns

The production of raw potassium salts from various brines in various conditions of Kara-Bogaz-Gol Gulf had been studied by Lepeshkov and Fradkina, 1959; Sedel'nikov, 1968; Nuryagdyev, Pasev'eva and Elomanova, 1984; Pasev'eva, Khodzhamamedov and Grishchenko, 1991; Atadjanov and Kurilenko, 1991; Atadjanov, Pasev'eva and Khodzhamamedov, 1995. It was found that the precipitated salts with composition given in Table 14 are formed from various raw materials (mirabilite mother brine, buried brines, surface brines before dam construction) when evaporating to the potassium content 1.20-1.25%. The technology of processing raw potassium salts into potassium fertilizers was developed by Pasev'eva and others, 1986; Pasev'eva, Khodzhamamedov and Grishchenko, 1991. For developing an efficient method for mineral production, the experimental data of salt solubility in five-components system K^+, Na^+, Mg^{2+}, Cl^-, SO_4^{2-} - H_2O at temperatures 25, 40, 55 and 75°C (Kaschkarov, Pasev'eva and Nuryagdyev, 1975; Nuryagdyev, Pasev'eva and Elomanova, 1981; Pasev'eva, Nuryagdyev and Kaschkarov, 1977, 1978) was used. The above range includes the compositions of raw potassium salt obtained by us in the process of solar evaporation of surface brine and of mirabilite mother brine. Therefore, the technology

developed earlier for production of potassium sulfate and other potassium fertilizers can also be used for investigating new raw materials.

The technology for producing potassium sulfate from raw potassium salt entails processing raw potassium salt and potassium regeneration from lye in the following two main steps:

a) Schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) is formed by interaction of raw potassium salt containing kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$), carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) and magnesium sulfate ($MgSO_4 \cdot kH_2O$) with water as per below reactions:

$$nKCl \cdot MgSO_4 \cdot 3H_2O + mH_2O \rightarrow K_2SO_4 \cdot MgSO_4 \cdot 6H_2O\downarrow + \text{schoenite lye} \quad (12)$$

$$nKCl \cdot MgCl_2 \cdot 6H_2O + mMgSO_4 \cdot kH_2O \rightarrow K_2SO_4 \cdot MgSO_4 \cdot 6H_2O\downarrow + \text{schoenite lye} \quad (13)$$

The obtained pulp is separated by filtration onto schoenite and schoenite lye, which is the mother solution left after the schoenite crystallization. A one step process yields 10-15% schoenite. To increase yield, a two-step process is employed by adding several parts water. In the first step, the quantity water added to raw potassium salt suffices for the formation of kainite from carnallite:

$$KCl \cdot MgCl_2 \cdot 6H_2O + MgSO_4 \cdot kH_2O + pH_2O \rightarrow KCl \cdot MgSO_4 \cdot 3H_2O\downarrow + \text{kainite lye} \quad (14)$$

In the second step, the kainite is decomposed by water according to reaction (12). In this process, the potassium yield in schoenite reaches 60-65% (Pasev'eva and others, 1986).

Processing schoenite and kainite lyes (the later lye is the mother solution left after the kainite crystallization) for potassium regeneration is conducted by a two-phase evaporation process of lyes mixture. In the first step of evaporation, halite and some of the water are removed. The mother solution is divided into two flows: one flow is replaced by water, while the second undergoes the second evaporation step in which water is removed and salt identical to initial raw potassium salt is crystallized. Then this salt is returned to the first step. The mother solution constitutes of the concentrated chloride-magnesium brine, which is proposed for production of bischofite and magnesium chlorite defoliant.

The optimal conditions for converting raw potassium salt into schoenite are the following: salt decomposition at 70-75°C for 15-20 minutes, pulp cooling to 35-40°C for 30-35 minutes, solid/liquid phase ratio for salt decomposition by water 1:(0.13-1.20) and by mother solution 1:1.50. The degree of potassium extraction from schoenite in the closed cycle reached 90-95% (Elomanova and Pasev'eva, 1993).

The production of potassium sulfate is based on schoenite decomposition by water. By using the one-step process, the mixture of potassium sulfate and leonite is formed. By adding more water, potassium sulfate almost pure of leonite can be obtained. However, this decreases significantly the yield of potassium sulfate in the final product. Therefore, to circumvent this process, the schoenite decomposition is conducted in two stages. At the first stage of conversion the decomposition of schoenite is conducted by sulfate solution of leonite (L) from the second stage of conversion (the production of this solution will be shown below). At this stage the precipitate, containing the mixtures of potassium sulfate and leonite, and the mother solution are formed:

$$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + K_2SO_4 + xH_2O \rightarrow K_2SO_4 \cdot MgSO_4 \cdot 4H_2O\downarrow + K_2SO_4\downarrow + \text{mother solution} \quad (15)$$

At the second stage of the conversion the obtained solid phase is decomposed by water with the formation of solid phase containing potassium sulfate and the mother (sulfate) solution L according to the reaction:

$$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O\downarrow + K_2SO_4\downarrow + yH_2O \rightarrow K_2SO_4\downarrow + \text{mother solution L} \quad (16)$$

The optimal conditions of this process are the following: temperature 45-50°C, process duration 45-50 minutes and continues mixing. With the purpose of the utilization of potassium sulfate the regeneration of the formed mother solutions by evaporation of the water excess was provided. At this process leonite and mother solution are formed: the formed leonite is returned to the first conversion step and the mother solution is moved into evaporative pond of raw potassium salt.

5. Development of technology for production of magnesium chlorate from surface bitterns

Kul'maksimov et al., 1986, Kul'maksimov and Tukhtaev, 1989, developed the method of producing chlorate-magnesium defoliant. This method used the chloride-magnesium brine left after the evaporation of potassium lyes of buried brines in the KBG Gulf. This method differs from the technology based on fusion of bischofite and sodium chlorite (Eqn. 17) at 130-140°C:

$$MgCl_2 + 2NaClO_3 \rightarrow Mg(ClO_3) + 2NaCl \quad (17)$$

The defoliant obtained by the later method contains sodium chloride, which is accumulated in soil and leads to its salinization. The data presented in Table 15 shows that the compositions of chloride-magnesium brines obtained at the processing of buried and surface solutions are identical. Therefore, we can use the developed technology in complex processing of surface brines.

V. Conclusions

a. Crystallization of surface brines at Kara-Bogaz-Gol Gulf by solar water evaporation has been experimentally studied.
b. Modeling isothermal evaporation of a solution, resembling the composition of the surface brines of Kara-Bogaz-Gol, was done by using the model developed by Prof. Krumgalz.
c. It was demonstrated that the results of model calculations correspond with experimental data.
d. The possibility of replacing buried brines by surface brines for production of sodium sulfate and other valuable products was substantiated.
e. Based on experimental and calculated data of evaporation of surface KBG brines, the crystallization paths were studied and the technology of complex processing of surface Kara-Bogaz-Gol brines was developed.

VI. Recommendations for industrial implementation of the developed technology

For the application of the developed technology of complex processing of surface Kara-Bogaz-Gol brines to industrial production it is necessary to carry out serious additional studies related to the development of new processes, reconstruction and modernization of the existing plants.

a. To develop the basic data for designing of technology of complex processing of surface brines of Kara-Bogaz-Gol Gulf.
b. To develop the technical and economic assessment of complex processing of surface brines of Kara-Bogaz-Gol Gulf.
c. To conduct the marketing study for various products (sodium sulfate, potassium sulfate, epsomite, bischofite, halite, etc.), this can be produced at complex processing of surface brines of Kara-Bogaz-Gol Gulf.
d. To work out the reconstruction plan of the pond system of the plant "Karabogazsulfat".
e. To prepare the basic data for general reconstruction and modernization of the plant "Karabogazsulfat".
f. To develop the investment strategy for the realization of the developed technology of complex processing of surface brines of Kara-Bogaz-Gol Gulf.

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VIII. TABLES

Table 1. Water balance of Kara-Bogaz-Gol for 1996-2001

Year	Gulf surface, km^2	Year average level (MSL), m	Seawater input, km^3/year	Rain input *, km^3/year	Water evaporation, km^3/year **	Water balance, km^3/year	Gulf volume, km^3
1995	18,400	-27.96	52.2	2.1	22.5	+32.8	90.9
1996	18,600	-27.36	25.3	2.1	22.5	+4.9	95.8
1997	18,600	-27.50	17.7	2.1	22.5	-2.7	93.1
1998	18,600	-27.40	18.0	2.1	22.5	-2.4	90.7
1999	18,600	-27.54	18.5	2.1	22.5	-1.9	88.8
2000	18,600	-27.58	18.9	2.1	22.5	-1.5	87.3
2001	18,600	-27.69	17.8	2.1	22.5	-2.6	84.7

* The annual volume of rains was regarded as average for many years.

** Water evaporation from the lagoon bittern surface depends on brine mineralization and was regarded as about 1.1 m/year (Lepeshkov et al., 1981).

Table 2. Coordinates of sampling stations (Fig. 2).

№	Place of sampling	Coordinates
1	Karasukut Canal (a zone of the gulf closet to the plant)	N41°38', E52°43'
2	Karasukut dam (a zone of the gulf closet to the plant)	N41°37', E52°44'
3	Sartas (Northwest zone of the gulf – approximately 600 m from the coastal line)	N41°48', E52°57'
4	Central zone of Kara-Bogaz-Gol	N41°28', E53°23'
5	Central zone of Kara-Bogaz-Gol	N41°10', E54°01'

Table 3. The physical properties and ionic composition of Kara-Bogaz-Gol surface and buried brines

Place of sampling	Date of sampling	Temp., °C	Density, g·cm^{-3}	pH	Ionic concentration, mass. %								B_2O_3, g/m^3
					Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	SO_4^{2-}	CO_3^{2-}	
Kurguzyl Bay *,	8.04.00	13.0	1,187		6.48	0.093	1.22	0.03	11.89	0.05	3.13	0.01	91
41°33′00″N	10.05.00	17.0	1,187		6.97	0.080	0.98	0.03	11.90	0.02	2.44	0.01	95
53°02′23″E	20.06.00	25.0	1,208		8.11	0.083	1.00	0.03	13.08	0.02	3.31	0.01	87
	20.07.00	26.3	1,192		7.17	0.118	1.01	0.03	11.99	0.02	2.90	0.01	101
	20.08.00	28.5	1,218		8.18	0.15	1.05	0.02	13.24	0.03	3.52	0.01	95
	20.09.00	19.7	1,213		8.10	0.134	1.11	0.02	13.08	0.03	3.78	0.01	107
	15.10.00	2.3	1,197		7.50	0.186	0.96	0.02	12.01	0.03	3.44	0.01	101
	18.11.00	9.6	1,195		7.49	0.137	1.02	0.02	12.16	0.04	3.40	0.01	88
	16.12.00	6.8	1,195		7.68	0.101	0.91	0.03	12.03	0.03	3.25	0.01	96
	18.01.01	6.5	1,199		6.83	0.102	1.07	0.03	11.56	0.03	3.01	0.01	77
	20.02.01	8.6	1,187		7.05	0.135	1.01	0.02	12.50	0.03	1.99	0.01	89
	15.03.01	8.9	1,184		7.09	0.128	1.07	0.02	12.57	0.03	2.19	0.01	90
	27.04.01	27.5	1,217		8.06	0.134	1.01	0.03	12.69	0.04	3.81	0.01	101
	27.05.01	19.1	1,212		8.22	0.124	1.09	0.03	12.99	0.03	4.04	0.01	108
	25.06.01	27.1	1,215		7.90	0.101	1.21	0.03	13.01	0.03	3.81	0.01	99
	19.07.01	23.6	1,210		7.18	0.101	1.21	0.03	12.27	0.03	3.31	0.01	114
	28.08.01	27.6	1,213		7.51	0.119	1.02	0.03	12.09	0.03	3.5	0.01	102
	20.09.01	17.5	1,212		8.04	0.090	1.10	0.03	13.01	0.03	3.64	0.01	88
	16.10.01	26.2	1,201		7.44	0.090	1.05	0.02	12.40	0.02	3.03	0.01	114
	20.11.01	18.5	1,195		7.09	0.109	1.11	0.03	11.78	0.02	3.4	0.01	89
	03.12.01	5.2	1,200		7.45	0.101	1.01	0.02	12.12	0.03	3.28	0.01	96
Sartas,	14.09.96		1,174		6.46	0.09	0.85	0.04	10.45	0.04	2.87	0	
41°46′26″N	26.09.98		1,192		7.59	0.12	0.99	0.03	12.18	0.04	3.43	0	
52°46′51″E	9.09.99		1,208		8.09	0.13	1.02	0.03	12.86	0.04	3.74	0	
	21.09.00		1,214		9.23	0.13	0.96	0.03	11.92	0.04	3.20	0	
	30.11.01		1,206		8.13	0.12	1.06	0.03	11.98	0.04	3.31	0	
Center zone, 41°15′00″N	26.01.01	6.1											
53°00′00″E, Depth 1 m													
2m			1,183	7.34	7.54		1.10	0.027	13.09	0.044	1.70	0	
3m			1,185	7.42	7.80		1.06	0.026	13.45	0.044	1.60	0	
4m			1,187	7.43	7.82		1.05	0.025	13.47	0.044	1.60	0	
5m			1,189	7.46	8.21		1.10	0.026	13.79	0.044	2.14	0	
6m			1,190	7.47	9.03		1.12	0.026	14.85	0.044	2.49	0	
			1,195	7.58	10.23		1.10	0.026	16.48	0.044	2.71	0	

Well #15	24.09.00		1,220		6.87	0.13	1.51	0.03	11.06	0.03	5.51	0	
Well #23	10.10.01		1,182		6.28	0.085	0.93	0.03	10.19	0.02	2.99	0.01	

* The point for sampling was situated near the plant pipeline supply entrance.

Table 4. Composition of surface brines of Kara-Bogaz-Gol

Sampling date	Ionic composition, molality									I_m
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	Br^-	HCO_3^-	$B_4O_7^{2-}$	SO_4^{2-}	
14.05.02	4.849	0.0400	0.5597	0.0740	4.872		0.0100		0.5128	7.045
07.08.02	4.882	0.0405	0.5732	0.0680	4.877		0.0100		0.5455	7.156
09.10.02	4.692	0.0397	0.5610	0.0730	4.581		0.0099		0.5246	6.848
27.11.02*	4.204	0.0400	0.5788	0.0650	4.582		0.0107		0.2807	6.150
13.06.03	4.401	0.0382	0.5657	0.0067	4.643	0.0199	0.0096	0.0009	0.5351	6.771
10.10.03	4.372	0.0380	0.5620	0.0066	4.612	0.0198	0.0095	0.0008	0.4625	6.588
10.11.03	4.059	0.0351	0.5236	0.0078	4.266	0.0156	0.0093	0.0008	0.3642	5.983

* The precipitation of mirabilite occurred (composition of sediment, % wt.: Na_2SO_4 30.12, $MgCl_2$ 0.311, KCl 0.017, NaCl 1.04)

Table 5. Drainage of Caspian Sea water to Kara-Bogaz-Gol for 1992-2003

Year	Water volume, km^3
1992	11.3
1993	36.6
1994	40.8
1995	52.2
1996	25.1
1997	17.7
1998	18.0
1999	18.5
2000	19.4
2001	18.0
2002	13.7
2003	15.8

Table 6. Air and brine temperatures during the process of solar evaporation experiment of surface brine

Temperature, °C	Brine	Air
Minimal	22	29
Maximal	41	41
Average in the morning (10 A.M.)	28	35
Average in the afternoon (4 P.M.)	36	38
Average for a day	32	36

Table 7. Ionic composition of liquid and solid phases formed during solar evaporation of surface brine (experimental data)

Brine	Ionic composition of liquid phase, molality									I_m
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	Br^-	HCO_3^-	$B_4O_7^{2-}$	SO_4^{2-}	
Surface brine	4.7716	0.0401	0.6114	0.0067	5.0643	0.0182	0.0102	0.0008	0.4458	7.0802
1	4.5067	0.0748	1.0715	0.0042	5.3078	0.0158	0	0.0014	0.8090	8.7218
2	3.4210	0.1436	1.7342	0	5.2028	0.0165	0	0.0032	1.0603	9.9812
3	2.8626	0.2090	2.5936	0	5.2436	0.0159	0	0.0049	1.3976	12.1479
4	2.1821	0.2417	2.9908	0	5.6972	0.0192	0	0.0063	1.3094	12.6705
5	0.6991	0.4841	4.2768	0	7.8893	0.0303	0	0.0940	0.8288	14.7627
6	0.4409	0.0527	5.6757	0	10.2302	0.0424	0	0.0150	0.6793	18.0931
7	0.4151	0.0260	5.8768	0	10.8842	0.0566	0	0.0176	0.4587	18.3619

Brine	Ionic composition of solid phase, % wt.								
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	Br^-	HCO_3^-	$B_4O_7^{2-}$	SO_4^{2-}
1	38.63	0.037	0.11	0.123	55.65	0.386	0	0.0156	1.17
2	34.54	0.074	1.31	0.08	44.55	0.31	0	0.0173	10.4
3	36.11	0.107	1.62	0	43.95	0.307	0	0.021	9.98
4	25.78	0.123	4.36	0	23.31	0.172	0	0.023	31.6
5	13.31	0.284	6.51	0	20.22	0.145	0	0.025	24.64
6	5.44	6.964	8.16	0	25.94	0.224	0	0.081	17.62
7	0.67	0.515	10.47	0	26.3	0.244	0	0.066	9.36

Table 8. Ionic composition of liquid phase formed during isothermal evaporation of surface brine (calculated data)

Brine	Ionic composition of liquid phase, molality								I_m
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	Br^-	HCO_3^-	SO_4^{2-}	
Surface brine	4.7080	0.0401	0.6114	0.0067	5.0643	0.0182	0.0102	0.4458	7.0482
1	4.9927	0.0649	0.9892	0.0014	5.5834	0.0294	0.0118	0.7070	8.7363
2	3.7877	0.0933	1.7408	0.0012	5.5627	0.0600	0.0240	0.8591	9.9660
3	1.8405	0.1082	3.0738	0.0014	6.0061	0.1175	0.0470	0.9647	12.1391
4	1.5303	0.1117	3.3450	0.0012	6.1553	0.1289	0.0516	1.0012	12.6856
5	0.6315	0.1456	4.3546	0.0005	7.3190	0.1845	0.0738	0.9550	14.7975
6	0.0841	0.0241	5.9844	0.0005	11.4593	0.3335	0.1335	0.0759	18.1390
7	0.0787	0.0216	6.0663	0.0006	11.5488	0.3922	0.1570	0.0681	18.3690

Table 9. Mineral content (% wt.) in solid phase being in equilibrium with proper brine (experimental data)

I_m	Gypsum	Halite	Bloedite	Epsomite	Carnallite	Kainite	Hexahydrite	Bischofite	Water
7.05									
8.74	0.52	98.9							0.60
9.97	0.07	81.9	18.03						
12.14		82.4	16.64						1.00
12.69		40.3	59.63						0.09
14.80		34.2		65.81					0.02
18.14		10.6			41.99	11.35	36.10		
18.37		2.77			3.88		22.81	66.27	4.27

Table 10. Mineral content (% wt.) in solid phase being in equilibrium with proper brine (calculated data)

I_m	Valerite	Glauberite	Halite	Glazerite	Bloedite	Anhydrite	Epsomite	Polyhalite	Hexahydrite	Kieserite	Carnallite	Bischofite
7.05												
8.74	0.77	1.27	**97.96**									
9.97		0.10	**77.77**	0.98	21.10							
12.14		0.003	**70.39**	0.98	27.62	0.01						
12.69			**69.28**	2.12	28.21	0.39						
14.80			**44.45**	0.80	5.93	0.07	34.47	0.02	14.26			
18.140			**16.07**					0.03	18.20	48.12	17.58	
18.37			**0.60**							1.48	0.95	96.97

Table 11. Ionic composition of initial liquid phase and mineral content in solid phases formed during mirabilite precipitation from Kara-Bogaz-Gol brines

Brine	Ionic composition of liquid phase, molality							I_m	Mineral content (% wt.) in solid phase		
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	SO_4^{2-}		Mirabilite	Halite	H_2O
Initial surface brine	4.6961	0.0406	0.5760	0.0740	4.8602	0.0099	0.5143	6.999	98.45	0.65	0.9
Evaporated brine	5.2799	0.0451	0.6514	0.0069	5.4608		0.5827	7.875	94.93	5.03	0.06

Table 12. Ionic composition of liquid phase formed during "solar" evaporation of mirabilite mother solution

Brine	Ionic composition of liquid phase, molality						I_m
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	
Mirabilite mother solution	4.5029	0.0420	0.5942	0.036	5.1799	0.2235	6.5109
1	4.7192	0.0491	0.7225	0.0081	5.5843	0.2760	8.1895
2	4.5698	0.0604	0.9348	0.0089	5.7031	0.3484	7.7508
3	4.5561	0.0832	0.1356	0.0089	5.7449	0.4074	8.2360
4	3.5142	0.1357	1.7806	0.0098	5.7398	0.6540	9.5837
5	2.4866	0.1618	2.2831	0.0042	5.5596	0.8375	10.3537
6	1.4597	0.2591	3.4994	0.0044	6.0735	1.2699	13.4428
7	0.4766	0.4002	3.9921	0.0044	7.0047	0.9231	13.7798
8	0.1111	0.4805	4.6299	0.0000	8.3082	0.7744	15.2586
9	0.1061	0.0784	5.2205	0.0000	9.3681	0.6303	16.4780

Table 13. Mineral content (% wt.) in solid phase being in equilibrium with proper brine ("solar" evaporation of mirabilite mother solution)

I_m	Gypsum	Halite	Bloedite	Epsomite	Carnallite	Tetrahydrite	Bischofite	Water
6.5109								
8.1895	0.40	99.4						
7.7508	0.12	99.1						
8.2360	0.09	99.8						
9.5837	0.02	99.8						
10.3537	0.03	99.6						
13.4428	0.01	99.8						
13.7798		25.5	19.24			51.87		3.4
15.2586		25.5		75.0				
16.4780				32.11	43.59		14.37	9.96

Table. 14. The composition of the raw potassium salt obtained by various methods from the Kara-Bogaz-Gol brines

Source of raw potassium salt	Composition of the raw potassium salt, %					
	NaCl	KCl	$MgSO_4$	$MgCl_2$	Insoluble residual	H_2O
Range of composition changes of various raw materials (literature data)	7.56-30.0	13.63-18.91	21.87-32.63	13.81-5.30	1.98-2.64	
Buried brine: industrial processing	7.50	17.58	22.22	12.33		39.58
Surface brine: our data related to solar evaporation	26.67	14.05	27.46	5.51		26.31
Surface brine: our data related to solar evaporation of mirabilite mother solution	10.90	14.69	24.51	14.39		35.51

Table. 15. Composition of chloride-magnesium brine obtained from the Kara-Bogaz-Gol Gulf brines

Source of the chloride-magnesium brine	The composition of chloride-magnesium brine, % wt.				
	NaCl	KCl	$MgSO_4$	$MgCl_2$	H_2O
Buried brine	0.28	0.21	3.78	32.22	63.51
Surface brine	0.09	0.12	3.47	32.42	63.90

Fig. 1. Levels of Caspian Sea and Kara-Bogaz-Gol from 1996 till 2001.

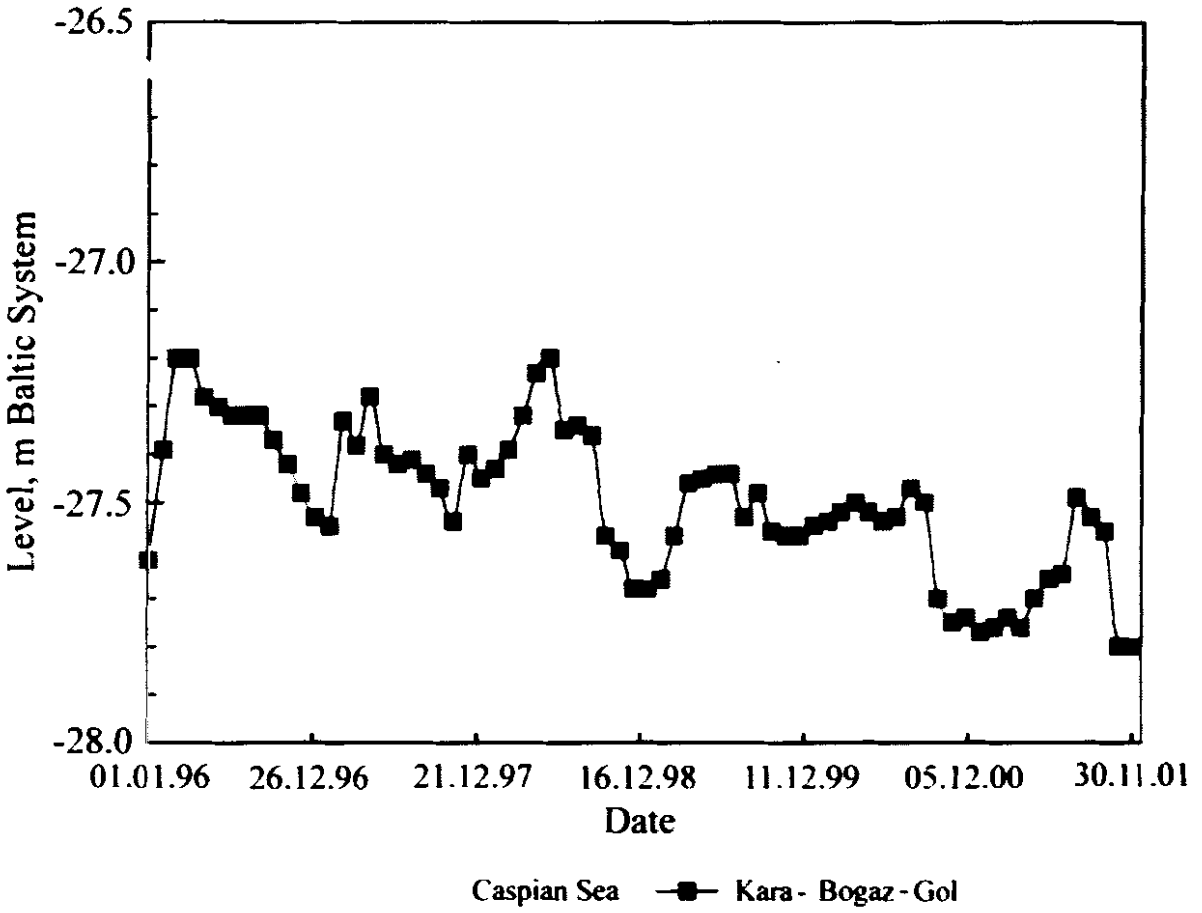


Fig. 2. Map of sampling locations.

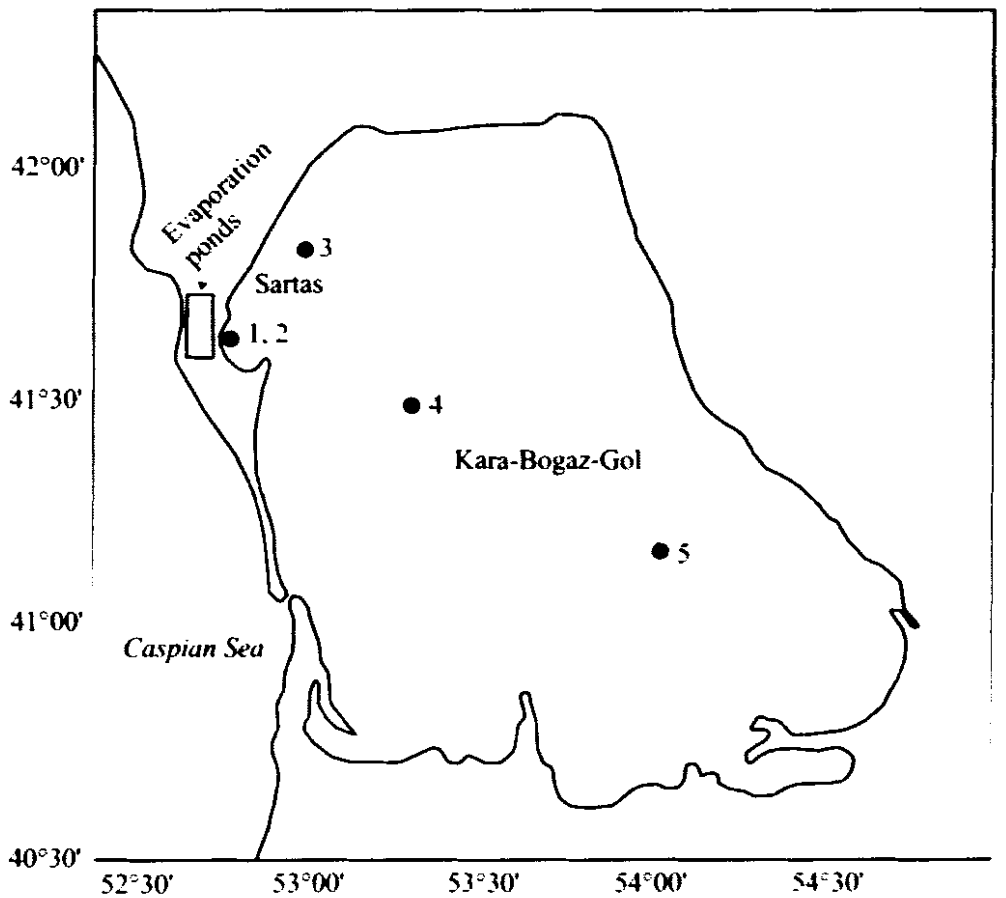


Fig. 3. Ionic concentration changes for the solar evaporation of Kara-Bogaz-Gol surface brine: points are the experimental data; lines are the calculated (modeling) data.

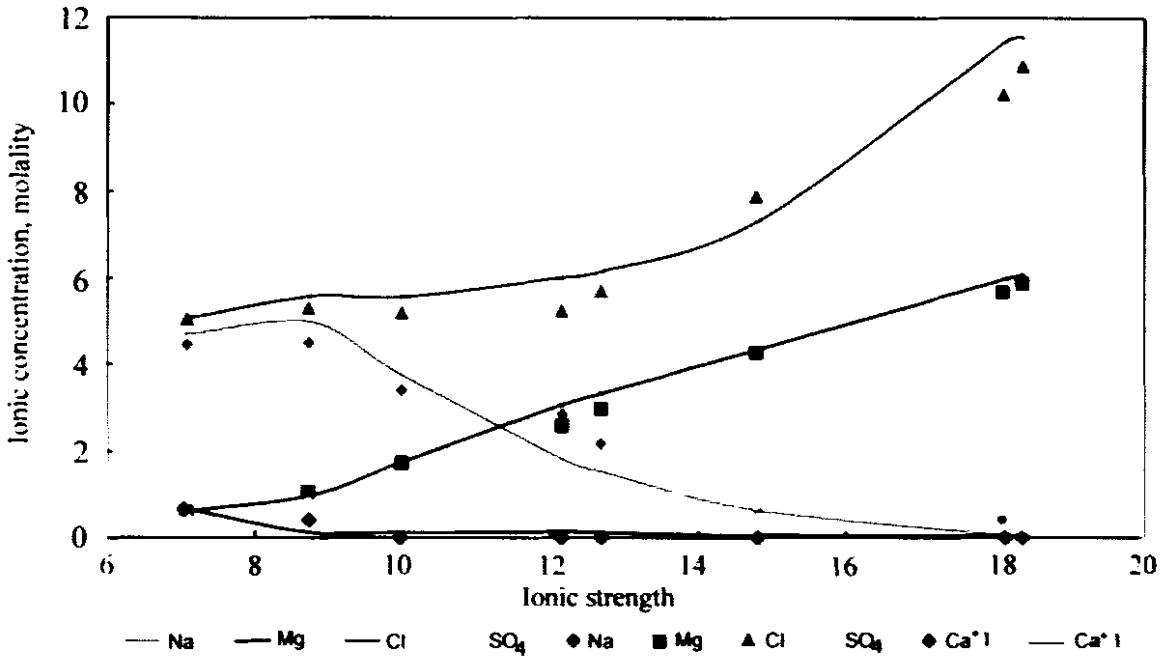
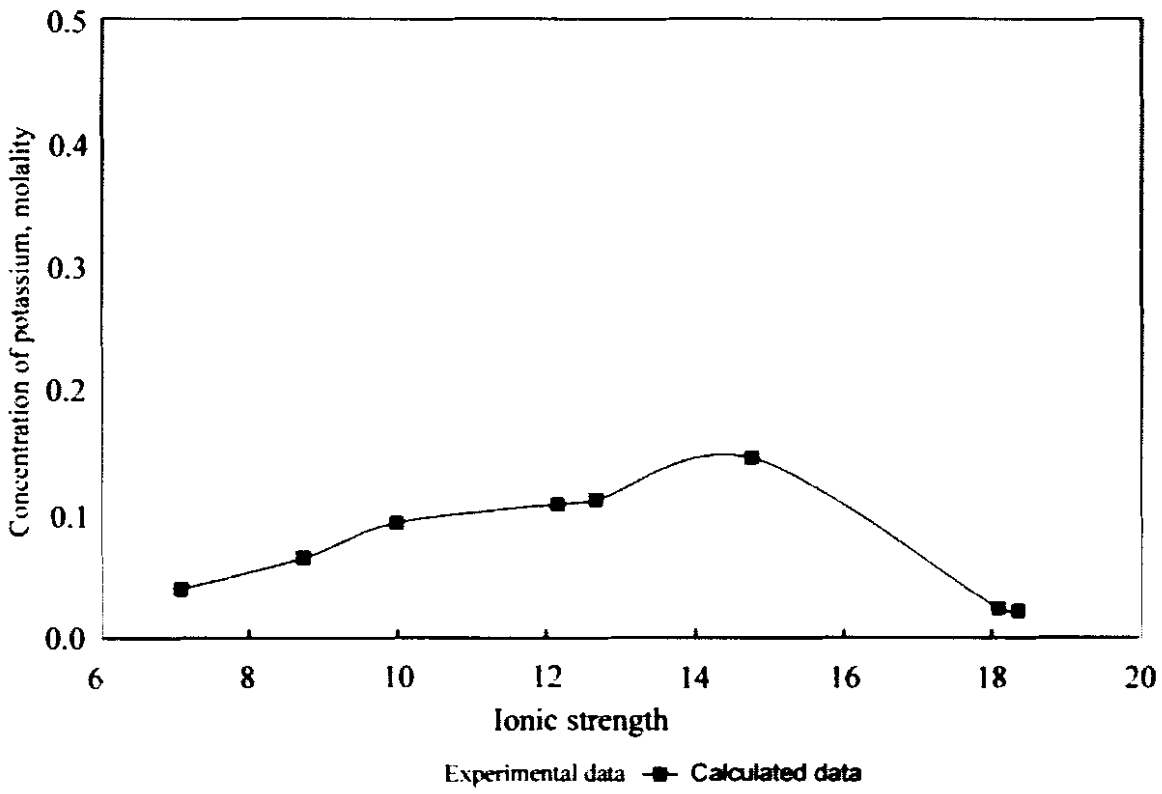


Fig. 4. Potassium ionic concentration changes for the solar evaporation of Kara-Bogaz-Gol surface brine: points are the experimental data; lines are the calculated (modeling) data.



X. APPENDIX.

Table 1A. Thermodynamic solubility products (K_{sp}) of minerals formed from major ions of natural waters at 25°C.

Mineral or chemical name	Formula	K_{sp}	References
Anhydrite	$CaSO_4$	$4.346 \cdot 10^{-5}$	Harvie et al., 1984
Antarcticite	$CaCl_2 \cdot 6H_2O$	$1.3917 \cdot 10^{4}$	Harvie et al., 1984
Arcanite	K_2SO_4	$1.674 \cdot 10^{-2}$	Harvie et al., 1984
Barite	$BaSO_4$	$1.112 \cdot 10^{-10}$	Robie et al., 1978
Bischofite	$MgCl_2 \cdot 6H_2O$	$2.854 \cdot 10^{4}$	Harvie et al., 1984
Bloedite	$Na_2Mg(SO_4)_2 \cdot 4H_2O$	$4.501 \cdot 10^{-3}$	Harvie et al., 1984
Calcium chloride tetrahydrate	$CaCl_2 \cdot 4H_2O$	$5.213 \cdot 10^{5}$	Harvie et al., 1984
Carnallite	$KMgCl_3 \cdot 6H_2O$	$2.140 \cdot 10^{4}$	Harvie et al., 1984
Celestite	$SrSO_4$	$2.333 \cdot 10^{-7}$	Reardon & Amstrong, 1987
Chloromagnesite	$MgCl_2$	$9.813 \cdot 10^{21}$	Pabalan and Pitzer, 1987
Epsomite	$MgSO_4 \cdot 7H_2O$	$1.315 \cdot 10^{-2}$	Harvie et al., 1984
Glaserite=aphthitalite	$NaK_3(SO_4)_2$	$1.576 \cdot 10^{-4}$	Harvie et al., 1984
Glauberite	$Na_2Ca(SO_4)_2$	$5.697 \cdot 10^{-6}$	Harvie et al., 1984
Gypsum	$CaSO_4 \cdot 2H_2O$	$2.628 \cdot 10^{-5}$	Harvie et al., 1984
Halite	$NaCl$	$3.719 \cdot 10^{1}$	Harvie et al., 1984
Hemihydrate	$CaSO_4 \cdot 0.5H_2O$	$1.846 \cdot 10^{-4}$	Marshall and Slusher, 1968
Hexahydrite	$MgSO_4 \cdot 6H_2O$	$2.317 \cdot 10^{-2}$	Pabalan and Pitzer, 1987
Hydrophilite	$CaCl_2$	$8.247 \cdot 10^{11}$	Robie et al., 1978
Kainite	$KMgClSO_4 \cdot 3H_2O$	$6.419 \cdot 10^{-1}$	Harvie et al., 1984
Kieserite	$MgSO_4 \cdot H_2O$	$7.541 \cdot 10^{-1}$	Harvie et al., 1984
Labile salt	$Na_4Ca(SO_4)_3 \cdot 2H_2O$	$2.128 \cdot 10^{-6}$	Harvie et al., 1984
Leonhardtite	$MgSO_4 \cdot 4H_2O$	$1.298 \cdot 10^{-1}$	Pabalan and Pitzer, 1987
Leonite	$K_2Mg(SO_4)_2 \cdot 4H_2O$	$1.050 \cdot 10^{-4}$	Harvie et al, 1984
Magnesium bromide hexahydrite	$MgBr_2 \cdot 6H_2O$	$2.028 \cdot 10^{5}$	Balarew et al., 1993
Magnesium chloride hydrate	$MgCl_2 \cdot H_2O$	$1.716 \cdot 10^{16}$	Pabalan and Pitzer, 1987
Magnesium chloride dihydrate	$MgCl_2 \cdot 2H_2O$	$7.493 \cdot 10^{12}$	Pabalan and Pitzer, 1987
Magnesium chloride tetrahydrate	$MgCl_2 \cdot 4H_2O$	$2.675 \cdot 10^{7}$	Pabalan and Pitzer, 1987
Magnesium sulfate	$MgSO_4$	$1.085 \cdot 10^{5}$	Pabalan and Pitzer, 1987
Mirabilite	$Na_2SO_4 \cdot 10H_2O$	$5.920 \cdot 10^{-2}$	Harvie et al., 1984
Pentahydrite	$MgSO_4 \cdot 5H_2O$	$5.190 \cdot 10^{-2}$	Pabalan and Pitzer, 1987
Pentasalt	$K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$	$2.759 \cdot 10^{-25}$	Greenberg and Moller, 1989
Polyhalite	$K_2MgCa_2(SO_4)_4 \cdot 2H_2O$	$1.804 \cdot 10^{-14}$	Harvie et al, 1984
Potassium bromide	KBr	$1.343 \cdot 10^{1}$	Robie et al., 1978
Potassium magnesium bromide	$KBr \cdot MgBr_2 \cdot 6H_2O$	$3.480 \cdot 10^{5}$	Balarew et al., 1993

Schoenite (picromerite)	$K_2Mg(SO_4)_2 \cdot 6H_2O$	$4.704 \cdot 10^{-5}$	Harvie et al., 1984
Strontium bromide	$SrBr_2$	$3.433 \cdot 10^{12}$	Robie et al., 1978
Sylvite	KCl	7.941	Harvie et al., 1984
Syngenite	$K_2Ca(SO_4)_2 \cdot H_2O$	$3.563 \cdot 10^{-8}$	Harvie et al., 1984
Tachyhydrite	$Mg_2CaCl_6 \cdot 12H_2O$	$2.421 \cdot 10^{17}$	Harvie et al., 1984
Thenardite	Na_2SO_4	$5.159 \cdot 10^{-1}$	Harvie et al., 1984

Table 2A. The ion interaction parameters $\beta_{i,j}^{(0)}$, $\beta_{i,j}^{(1)}$, $\beta_{i,j}^{(2)}$ and $C_{i,j}^{\phi}$ at 25°C.

Cation	Anion	$\beta_{i,j}^{(0)}$, kg·mol^{-1}	$\beta_{i,j}^{(1)}$, kg·mol^{-1}	$\beta_{i,j}^{(2)}$, kg·mol^{-1}	$C_{i,j}^{\phi}$, kg^2·mol^{-2}	I_{max}	Reference
Na	Cl	0.0765	0.2664	-	0.00127	6	Pitzer & Mayorga, 1973
Na	Br	0.0973	0.2791	-	0.00116	4	Pitzer & Mayorga, 1973
Na	HCO_3	0.028	0.044	-	-		Peiper & Pitzer, 1982
Na	SO_4	0.01958	1.1130	-	0.004974	12	Pitzer & Mayorga, 1973
Na	CO_3	0.03622	1.51	-	0.00520		Peiper & Pitzer, 1982
K	Cl	0.04835	0.2122	-	-0.00084	4.8	Pitzer & Mayorga, 1973
K	Br	0.0569	0.2212	-	-0.00180	5.5	Pitzer & Mayorga, 1973
K	HCO_3	0.0296	-0.013	-	-0.008		Harvie et al., 1984
K	SO_4	0.04995	0.77925	-	0	2.1	Pitzer & Mayorga, 1973
K	CO_3	0.1488	1.43	-	-0.0015		Harvie et al., 1984
Mg	Cl	0.35235	1.6815	-	0.005192	13.5	Pitzer & Mayorga, 1973
Mg	Br	0.43268	1.75275	-	0.00312	15	Pitzer & Mayorga, 1973
Mg	HCO_3	0.033	0.84975	-	0		Pitzer et al., 1985
Mg	SO_4	0.2210	3.343	-37.23	0.0250	12	Pitzer & Mayorga, 1974
Mg	CO_3	2.833	-15.069	-204.9	-0.970		Millero & Thurmond, 1983
Ca	Cl	0.3159	1.6140	-	-0.000339	7.5	Pitzer & Mayorga, 1973
Ca	Br	0.3816	1.6132	-	-0.00257	6	Pitzer & Mayorga, 1973
Ca	HCO_3	0.39975	2.9775	-	0		Harvie et al., 1984
Ca	SO_4	0.20	3.1973	-54.24	0	0.044	Harvie et al., 1980
Sr	Cl	0.28575	1.66725	-	-0.0013	12	Pitzer, 1979
Sr	Br	0.33112	1.7115	-	0.00123	6	Pitzer & Mayorga, 1973
Sr	SO_4	0.220	2.88	-41.8	0.019		Pitzer, 1991
Ba	Cl	0.2628	1.49625	-	-0.01938	5.4	Pitzer, 1979
Ba	Br	0.31455	1.56975	-	-0.01596	6	Pitzer, 1979

Table 3A. Higher order interaction terms $\theta_{i,j}$ and $\psi_{i,j,k}$ at 25°C for Pitzer's equations with electrostatic terms.

Ions			$\theta_{i,j}$	$\psi_{i,j,k}$,	I_{max}	Reference
i	j	k	$kg \cdot mol^{-1}$	$kg^2 \cdot mol^{-2}$		
Na	K	*Cl*	-0.012	-0.0018	4.8	Pitzer & Kim, 1974
Na	K	Br	-0.012	-0.0022	4	Pitzer & Kim, 1974
Na	K	HCO_3	-0.012	-0.003		Harvie et al, 1984
Na	K	SO_4	-0.012	-0.010	3.6	Pitzer & Kim, 1974
Na	K	CO_3	-0.012	0.003		Harvie et al., 1984
Na	Mg	Cl	0.070	-0.012		Harvie & Weare, 1980
Na	Mg	SO_4	0.070	-0.015		Harvie & Weare, 1980
Na	Ca	Cl	0.070	-0.007		Pitzer, 1975
Na	Ca	SO_4	0.070	-0.055		Harvie et al., 1982
Na	Sr	Cl	0.051	-0.0021		Reardon & Armstrong, 1987
Na	Ba	Cl	0.067	-0.012		Pitzer, 1975
K	Mg	Cl	0	-0.022		Harvie & Weare, 1980
K	Mg	Br	0	-0.0265		Balarew et al., 1993
K	Mg	SO_4	0	-0.048		Harvie & Weare, 1980
K	Ca	Cl	0.032	-0.025		Pitzer, 1975
K	Ca	SO_4	0.032	0	0.7	Harvie & Weare, 1980
K	Sr	Cl	0.0149	-0.0201		Kim & Frederick, 1988b
K	Ba	Cl	0.010	-0.017		Pitzer, 1975
Mg	Ca	Cl	0.007	-0.012		Harvie & Weare, 1980
Mg	Ca	SO_4	0.007	0.024		Harvie et al., 1982
Cl	Br	Na	0.000	0.000	4.4	Pitzer & Kim, 1974
Cl	Br	K	0.000	0.000	4.4	Pitzer & Kim, 1974
Cl	HCO_3	Na	0.03	-0.015		Harvie et al., 1984
Cl	HCO_3	Mg	0.03	-0.096		Harvie et al, 1984
Cl	SO_4	Na	0.030	0.000		Pitzer, 1982
Cl	SO_4	K	0.030	-0.005		Pitzer, 1982
Cl	SO_4	Mg	0.030	-0.0080		Pabalan & Pitzer, 1987b
Cl	SO_4	Ca	0.030	-0.002		Pitzer, 1991
Cl	CO_3	Na	-0.02	0.0085		Harvie et al., 1984
Cl	CO_3	K	-0.02	0.004		Harvie et al. 1984
HCO_3	SO_4	Na	0.01	-0.005		Harvie et al., 1984
HCO_3	SO_4	Mg	0.01	-0.161		Harvie et al., 1984
HCO_3	CO_3	Na	-0.04	0.002		Harvie et al., 1984
HCO_3	CO_3	K	-0.04	0.012		Harvie et al., 1984
SO_4	CO_3	Na	0.02	-0.005		Harvie et al., 1984
SO_4	CO_3	K	0.02	-0.009		Harvie et al., 1984

XI. MANAGERIAL ISSUES

The current project had a very difficult "birth". The official agreement between the CDR-CAR administration and IOLR was signed only on 26th August 2001. The complex political situation in the region of Central Asian Republics at the time postponed the signing of the Subgrant to Grant No. TA-MOU-00-CA20-072 agreement between IOLR and Sci. Research Cooperation "GUN" (92 Esgerler St., Ashgabat, Turkmenistan) until the middle of the November 2001.

Prof. A. Khodjamamedov and Dr. N.N. Kazantseva had numerous problems in opening a new foreign currency account for this project. This account was opened only on the 17th of April 2002, about 8 months later than the project starting date: 1.08.2001. The first installment of the money was received only at the end of November, i.e., 16 months late. This situation led to the delay of the winter field sampling of water from the Kara-Bogaz-Gol, which was planned for September-October 2001, and the first water sampling in Kara-Bogaz-Gol, which should have been carried out during March-May 2002. The money required for equipment has not yet reached the Turkmenistan scientific team, even haft the time into the project duration.

XII. COLLABORATION AND TRAVEL

Both sides discussed in detail, scientific plans for fulfillment of the project, financial and scientific reports, results of experimental work and necessary future steps for successful fulfillment of the project.

XIII. ACKNOWLEDGMENT

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