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

H11/2003

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

I.O.L.R. REPORTS

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B

INTRODUCTION

The present annual report covers the period from August 2001 to November 2002. During this period, preliminary studies regarding evaporation of various waters from Kara-Bogaz-Gol were conducted. Among these stages, the following experiments were carried out:

a) The water sampling of surface brine from Kara-Bogaz-Gol for spring, summer and winter seasons was conducted and chemical analysis of brines was carried out.
b) The process of mirabilite precipitation from surface brine of Kara-Bogaz-Gol was studied.
c) We studied the process of solar evaporation of mirabilite mother water as a basis for complex technology of mineral production from surface brines.

The results obtained and problems that we met allowed us to choose and consequently order appropriative analytical equipment.

SCIENTIFIC SUMMARY

1. Seasonal changes for chemical composition of surface brines

1.1. Sampling places

The most available place for surface brine sampling was at the northwest shore zone closed to the existing mineral production plant. The sampling was conducted in a shore area approximately 500 m from a dam between Karasukut Bay, the central zone and in a canal which connected Karasukut Bay and the central zone (Fig. 1). 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, has a variable composition and the lowest salt concentrations. The highest mineralization was observed in central zone and the northwest coastal zone. The coordinates of sampling stations in these zones, which were used earlier and are also being utilized at present, are presented in Table 1. Statistical analysis of the chemical composition of Kara-Bogaz-Gol water from 1995 till the present shows that the composition of brines in the central zone, in Sartas Bay and approximately 500 m from a dam between Karasukut Bay and the central zone are almost identical. For these stations, at the same sampling period, the difference

between both concentrations of particular ions and total salts content is less then 5%. The data for comparison is presented in Table 2. All the above mentioned allowed us to consider that composition of brine sampled in 500 m from a dam between Karasukut Bay and the central zone is average for northwest shore zone.

Table 1. Coordinates of sampling stations (Fig. 1).

№	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′

1.2. Chemical analysis of brines

Brine samples after sampling were kept in glass bottles equipped with ground glass stoppers. Contents of major ions in the brines were determined in accordance with standard techniques as follows:

Cl^- concentration was determined by volumetric argentometric titration.

SO_4^{2-} concentration was determined by gravimetric analysis in the form of $BaSO_4$.

CO_3^{2-} and HCO_3^- concentrations was determined by volumetric titration using 0.05M HCl, phenolphtalein and methilorange as indicators.

Ca^{2+} and Mg^{2+} concentrations were determined by complexonometry analysis with murexid and chromogen black as indicators.

K^+ and Na^+ concentration was determined by the flame photometry method.

The relative precisions of the Cl^-, SO_4^{2-}, HCO_3^-, Ca^{2+}, Mg^{2+}, K^+ and Na^+ determination were as follows: 0.10%, 0.05%, 0.20%, 0.20%, 0.05%, 1.19%, 0.45%, respectively.

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

The physical properties and composition of the Kara-Bogaz-Gol surface brines and sediments are presented in Table 2. According to the data obtained, the concentration of

salts increased during the summer. The largest mineralization (26.12%) was observed in August. In November when temperature of the brine reached less then 10°C, precipitation of mirabilite occurred. At the present time, the shore zone is covered by layer of mirabilite containing a small quantity of halite and epsomite (Table 2). This year, winter came early and was very cold, and as a result, mirabilite precipitated before the average time. 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.

2. Mirabilite precipitation from surface brine

Since mirabilite production is the basis for the technology of mineral salts production from Kara-Bogaz-Gol brines by both pond and industrial methods we have investigated 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 the figurative brine composition point is situated in the field of halite crystallization and NaCl concentration is high. We suggest that mirabilite could precipitate together with halite. Such a precipitation is a negative technological factor.

Mirabilite precipitates by a slow decrease in brine temperature until it reaches 0°C. This process is the imitation of mirabilite production in industry. Mirabilite crystallizes without addition of any seed crystal. The pulp obtained was separated on Büchner funnel with the use of a vacuum pump.

A preliminary study of the process of mirabilite crystallization was carried out for 2 brines: surface brine and an evaporated surface brine (approximately 10% of the brine water evaporated). The second brine was used as concentration of salts in surfaces brine increased every year and we were curious as to the composition of mirabilite which can easily be produced in future. The composition of brines, sediments and mother waters are presented in Table 3. The analysis of the results obtained will allow us to develop a strategic plan for further study.

3. Solar evaporation of mirabilite mother water

Mirabilite precipitation is the first stage of a complex technology of surface brine processing. Therefore, mirabilite mother water is the initial raw material for production of other mineral salts and the process for mirabilite mother water preparation by the pond method is the basis of the future technology. The study of the process of solar evaporation of mirabilite mother water has been carried out to determine the conditions at 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.

Preliminary study of the process 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 close to natural conditions. A shallow glass vessel was filled with brine and put outside open place available for wind and sun. The temperature was measured every day at 9 a.m., 2 p.m. and 5 p.m. The average values for air and brine temperature were equal to 35°C in the morning and 39°C in the afternoon. The initial brine volume was equal to 3.0 dm^3. The separation of liquid and solid phases was conducted by vacuum filtration when approximately 10% of the water was evaporated or if new crystal in a solid phase was formed. The weight of liquid and solid phases was 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 finished when the eutectic point was reached. Crystal formation was determined by chemical analysis of the solid phases and suggested by graphic calculation using Schrainemaker's method for solubility diagrams of aqueous salt systems and microscope investigations.

Based on the results obtained in this preliminary study related to distribution of brine components between liquid and solid phases, brine composition suitable for industrial production of sulfates, sodium, potassium and magnesium chlorides and other valuable components could be chosen.

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MANAGERIAL ISSUES

The current project had a very difficult "birth" and a difficult growing period. The official agreement between the CDR-CAR administration and IOLR was signed only on the 26th August 2001. The complex political situation in the region of Central Asian Republics at that period of time postponed the signing 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 opening a new foreign currency account for this project. This account was opened only on the 17th of April with approximately an 8-month delay from the official date of the project starting date: 1.08.2001. The first portion of the money was obtained only at the end of November, i.e., with a delay of more than 16 months. This type of 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 would have been carried out during March-May 2002. The portion of money required for equipment purchase has not get reached the Turkmenistan scientific team even after more than half the period allocated for project fulfillment!

COLLABORATION AND TRAVEL

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

The business trip to Israel to coordinate the program of the project and to acquaint the Turkmenistan scientific team with analytical methods applied to highly mineralized brines was postponed for the spring of 2003.

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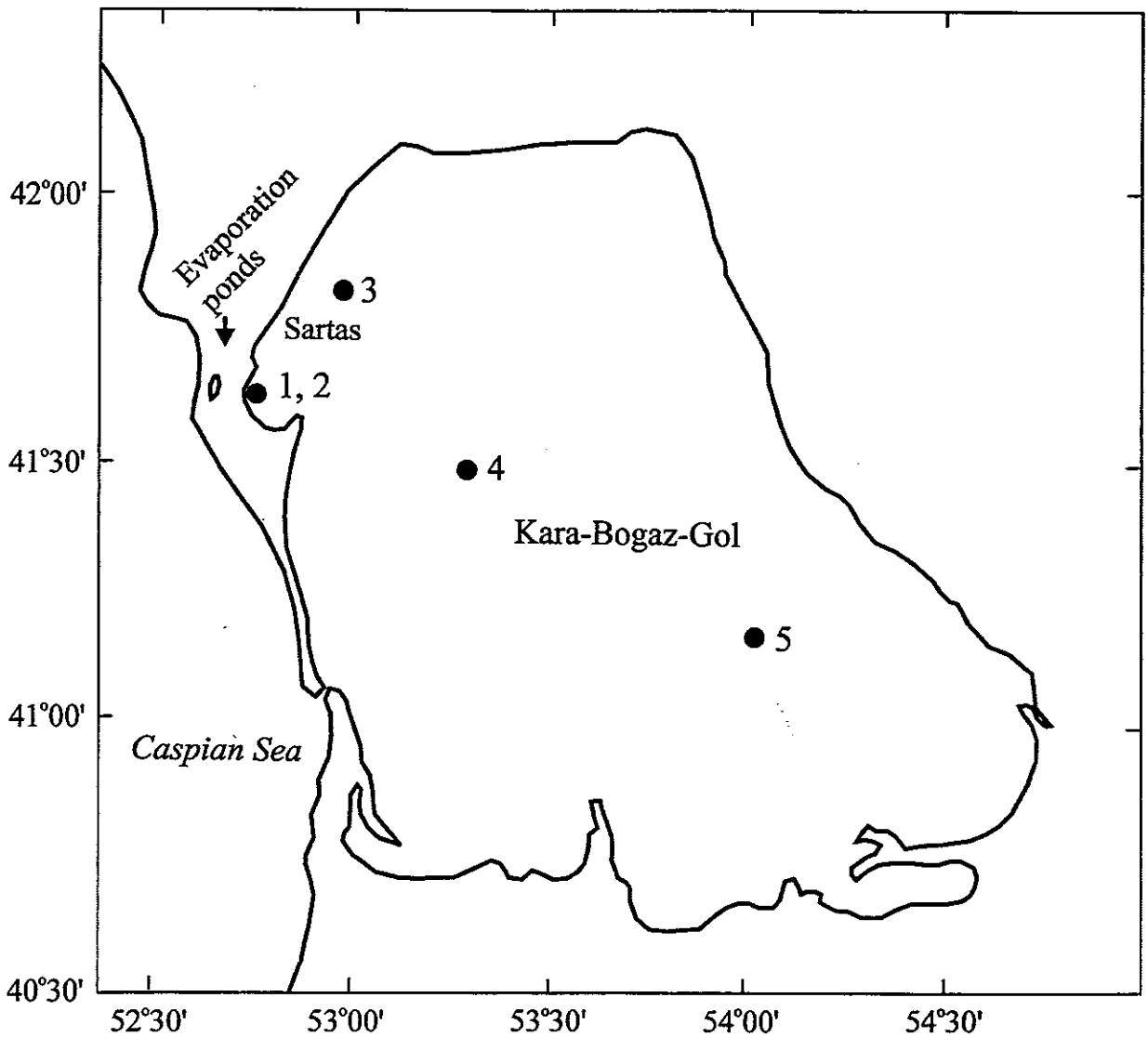

Fig. 1. Map of sampling locations