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Research Article

INVESTIGATION OF THE DYNAMICS OF CHEMICAL AND MINERALOGICAL COMPOSITION OF BRINE AND SOILS OF THE DRY BOTTOM OF THE ARAL SEA

Aktam Erkayev[1], Karjawbay Reymov[1], *Makset Medetov[2] and Bakhrom Kucharov[1]
[1]*Tashkent chemical-technological Institute, Uzbekistan, Tashkent*
[2] *Institute of Zoology, Science Academy of the Republic of Uzbekistan Tashkent, Uzbekistan*
**Author for Correspondence*

ABSTRACT
Based on the studies carried out, the patterns of distribution of clay materials and soluble salts in the soil of the strata of the western coast of the Big Aral Sea was established. According to chemical and physicochemical methods of studying water-soluble salts and water-insoluble soil residues was shown that the samples contain the following water-soluble minerals: mirabilite, thenardite, halite, bledite, konyavite, leveite, vanthoffite, pentahydrate, starkeite, sanderite and kieserite. The composition of the soil of the drained bottom of the Aral Sea and the settled dust in the city of Nukus from a salt-air storm has been established. The main part of the salt components consists of monoparticles of volatile thenardite (Na_2SO_4). A sequence of measures is proposed to prevent the negative impact of the global ecological catastrophe of the Aral Sea on the planet.

Keywords: *Aral Sea, Salt Formation, Salinity, Thenardite, Brine, Cyclochronogram*

INTRODUCTION
The Aral Sea is the fourth largest lake in the world and in size, is second only to the Caspian Sea, Lake Superior (the largest of the Great Lakes in North America) and Lake Victoria in Africa Over the past 20,000 years and until the middle of the last century the Aral Sea was a unique body of water among the sultry deserts of Central Asia and Kazakhstan. It had amazing properties of both the lake and the sea. The long-term mean sea level for the period of instrumental observations from 1911 to 1960 was 53 m above the zero of the Kronstadt foot gauge, taken as a reference point. The sea area was 68320.5 km^2, the maximum depth was 69 m, the average depth was 16.1 m. Interannual level fluctuations did not exceed 0.2-0.5 m.
The coastline was about 4430 km long. There were more than 1,100 islands in the Aral Sea. The average salinity was 10%, i.e. more than three times lower than the average salinity of the waters of the World Ocean. The ecosystem of the Aral Sea included hundreds of species of marine fauna and flora. The presence of a large reservoir had a softening effect on the climate, which turned the Aral Sea region into an oasis in the middle of the desert. But, in the early 1960s, the sea began to recede rapidly (Rubanov *et al*, 1987; Kurbanbaev *et al*, 2011; Zavyalov *et al*, 2012).
However, since the 60s of the twentieth century, natural and irreversible natural changes in the foreseeable future have been taking place here. The area of the water surface of the Aral Sea has decreased by more than 2/3, the initial sea level has decreased by 22 m, salinity has increased 6-12 times. The drained area of the former seabed was more than 62 thousand km^2. Several tens of millions of tons of salt dust are blown out from it every year. Lenses of fresh water are becoming scarce in the sandy soils of the islands and the coast. Increased mineralization and pollution of drinking water have put the Republic of Karakalpakstan on the brink of a humanitarian disaster.
By the beginning of the third millennium, the Aral Sea was divided into three residual water bodies: the Small Sea (area - 3092 km^2, level - 40.2 m, volume - 21.8 km^3), the Eastern shallow and Western deep

water parts of the Big Sea (area - 3687 km^2, level -31 m, volume-109 m^3). The Big Sea continues to shrink, but is already close to equilibrium. The Small Sea has stabilized, the Kokaral dam will help regulate its regime (Cretaux *et al,* 2005; Friedrich *et al,* 2004; Small *et al,* 2001; Zavialov *et al,* 2008; Zavialov *et al,* 2008; Erkaev *et al,* 2014; Erkaev *et al,* 2016).

In his speech at the 72nd session of the UN General Assembly, President Sh.M. Mirziyoyev once again drew the attention of the world community to the problem of the Aral Sea and stressed the need to unite efforts in this matter. In terms of its volume, the Aral Sea was the fourth lake in the world, famous for its flora and fauna. Unfortunately, over the past 58 years, the area of water has decreased 12 times. The salt content of the western deep-water part of the Big Aral Sea (ZGVCHBAM) in a liter of water is 130-150 grams. Today, on the site of the former sea, a sandy-salt desert with an area of more than 6.2 million hectares has formed with deposits of toxic pesticides.

According to scientists, up to 5 tons of dust and salt fall on each hectare of arable land in Karakalpakstan every year. The sand-salt storm that occurred on 05/27/18 showed how vulnerable the environment is to an ecological disaster. Dust storms lifted into the air, spreading toxic chemicals, harm the health of not only the local population, but also people from other countries, even continents.

Thus, the dried-up bottom of the Aral Sea, as a source of salt spread, has become a global threat.

Significant disturbances in the Aral Sea regime coincided in time with the changes that took place in the general circulation of the atmosphere and synoptic processes in Central Asia. In subsequent years, the Aral Sea continued to recede, and further changes were carried out in the general circulation of the atmosphere, which led to large climatic anomalies (Rubanov *et al,* 1987; Kurbanbaev *et al,* 2011; Zavyalov *et al,* 2012; Cretaux *et al,* 2005; Friedrich *et al,* 2004).

With the financial support of international organizations, expeditionary observations were intensified. This makes it possible to continue tracking the process of adaptation of micro or mesoclimatic characteristics in this so unique natural situation to global climatic fluctuations.

MATERIALS AND METHODS

The compositional and structural characteristics of the feedstock were studied using a scanning electron microscope (MA10, Carl Zeiss, Germany) with an energy-dispersive elemental analyzer (Oxford Instruments, Great Britain). The principle of SEM operation is to scan the sample surface with a focused electron beam and analyze the electrons reflected from the surface and the emerging X-ray radiation characteristic of each element as a result of the interaction of the electron beam with matter (Lyman *et al,* 1994; Goldstein *et al.,* 1981).

The change in the pH of the medium was monitored with an I-160MI universal ion meter equipped with an EVL-1M3.1 electrode and a TK-06 temperature sensor. The glass electrode was calibrated with standard buffer solutions prepared from standard dose rates pH = 1.68–9.18, corresponding to GOST 8.135-74 (Vasiliev *et al.,* 1989; Pavia *et al,* 2006; Skoog *et al,* 1996; Erkaev *et al,* 2019).

The identification of the samples was carried out on the basis of diffraction patterns, which were recorded on an XRD-6100 apparatus (Shimadzu, Japan) controlled by a computer. We used CuKα-radiation (β-filter, Ni, 1.54178 current mode and tube voltage 30 mAkV) and a constant detector rotation speed of 4 degmin with a step of 0.02 deg. (ω / 20-adhesion), and the scanning angle varied from 4 to 80 ° C (Lyman *et al,* 1994; Vasiliev *et al.,* 1989; Pavia *et al.,* 2006; Skoog *et al,* 1996; Erkaev *et al.,* 2019).

RESULTS AND DISCUSSION

From the analysis of literature data, it follows that the process of draining the bottom of the Aral Sea by salt loss has three zones, which are determined by the areas of gradual salt formation (Erkaev *et al,* 2014; Erkaev *et al.,* 2016).

Calculations show that in the Aral Sea the average salt content is 12968.408 million tons, i.e. the forecast error does not exceed ± 16%.

In contrast to the eastern one in the western basin of the Big Aral, all parameters change according to a certain functional dependence, which is explained by its deep water and the presence of a connection with the eastern basin through the Kuland overflow and groundwater (Zavyalov *et al.*, 2012). During the expedition on June 15-25, 2014 in the western basin of the Big Aral, sections were made from 45 ° 30 'to 44 ° 30' north latitude. western and eastern coasts, respectively. The deepest point (32.8 m) was observed at 45 ° 25 'north latitude, in each section, samples were taken from 7-8 points with a depth of 0; 10; 20; 30 m with direct on-site determination of salinity and temperature of samples. It has been established that the salinity of the surface of the water surface (depth 0 m) from north to south increases from 121-126 g / l with a temperature of 23-26 ° C to 145-150 g / l with a temperature of 26-31 ° C (44 ° 28 'north latitude). With an increase in depth from 0 to more than 30 m, salinity increases from 124-128 g / l at a temperature of 23-24 ° C to 136-144 g / l at a temperature of 4-11 ° C.

Vertical stratification is observed in all sections; the difference in salinity of the upper quasi-uniform and bottom layers reaches 5-21 g / l. This vertical salinity stratification provides pronounced thermoclines, which cause a temperature drop of 16-23 ° C at a depth of 0-20 m.

In the measurements of the expedition on July 19-26, 2016, although the wind speed is 6-8 m / s and the temperature in depth varies from 27.9 to 6.3 ° C (N-44 ° 58218; E-58 ° 19025) and from 26 to 5.1 ° C (N-45 ° 29678; E-58 ° 35456), but the salinity is at the same level, that is, complete convection (mixing) of the wind brine layers is provided throughout the equator.

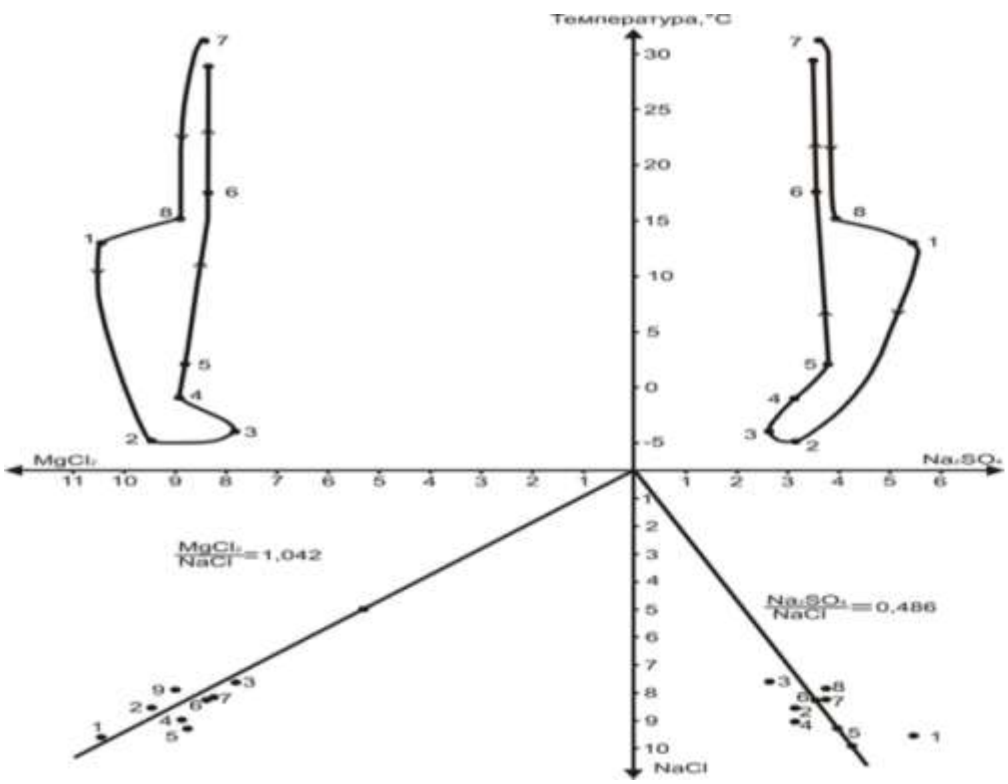

Figure 1: Cyclochronogram of the deep-water western part of the Great Aral Sea.

In Fig.1 the cyclochronogram reflects the annual change in the brine composition of the western deep-water part of the Big Aral Sea (ZGVCBAM) until 2019. TS-curves and cyclochronograms of ZGVChBAM of three water layers: surface, intermediate and bottom, differing in temperature and chemical composition, were obtained. The cyclochronogram shows that a decrease and an increase in temperature changes the cycle of sodium sulfate content in the brine clockwise, and the magnesium chloride content changes counterclockwise. Based on this, the ratio Na_2SO_4 / NaCl: $MgCl_2$ / NaCl is 0.40; 0.47; 0.48; and 0.77; 0.80; 1,041 respectively in 2012, 2013 and 2018.

The results of analyzes showed that in the composition of the water of the Great Aral Sea, the relative content of Cl^- in the dry residue increases from 34.5 to 51.93%, and the content of SO_4^{2-}, on the contrary, decreases from 31.1 to 14.99% (Table 1). Accordingly, the SO_4^{2-} / Cl^- ratio decreases from 0.9 to 0.29 simultaneously with an increase in salinity by 15-20 times.

Table 1: Relative contents (% by mass) of the main salt-forming ions in the water of the Big Aral in 1952, 2008 and 2019

Years	Cl^-	SO_4^{2-}	HCO_3^-	Mg^{2+}	K^+	Ca^{2+}	SO_4^{2-}/Cl^-
1952	34.50	31.10	1.50	5.20	1.,20	4.60	0.90
2008	43.30	22.60	0.60	6.70	1.48	0.50	0.52
2014	49.44	17.47	0.48	7.53	1.51	0.55	0.35
2018	51.30	16.10	0.48	8.80	1.52	0.63	0.32
2019	51.93	14.99	0.44	8.61	1.53	0.61	0.29

For 67 years from 1952 to 2019 the type of water changes from sulfate-chloride to chloride-sulfate, because when water evaporates with an increase in the content of the sum of salts and a decrease in temperature (in the winter season), a certain amount of mirabilite precipitates.

In the summer season, at temperatures above 5 °C, mirabalite almost completely dissolves, and at temperatures below 5 ° C at a depth of more than 20 m, it does not dissolve and the process of its accumulation takes place. The increase in water salinity also contributes to an increase in the proportion of precipitated mirabalite.

Due to these factors, the sulfate-chloride ratio (SO_4^{2-}/Cl^-), which is considered an important characteristic of the chemical type of the reservoir (Bortnik, Chistyaeva, 1990), decreased from 0.90 to 0.52 and 0.29, i.e. e. up to 42 and 68%, respectively, from 2008 to 2019 during the drying up of the Aral Sea. Thus, the brine ZGVChBAM approaches the chloride type, which is characteristic, in particular, of ocean waters.

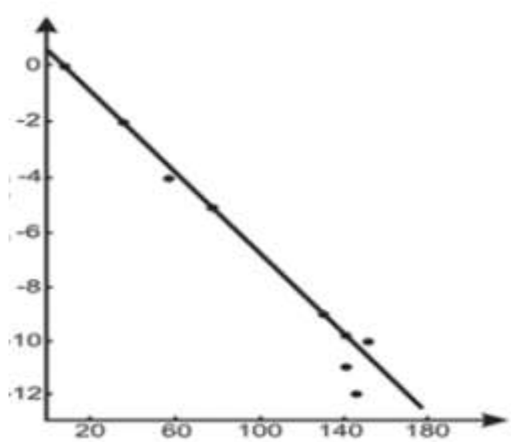

Figure 2: Dependence of the freezing point of the ZGVChBAM brine on salinity (2018 data)

The physicochemical properties of water bodies are of great importance for their characteristics, especially depending on the temperature and composition of the waters. For 2008-2019 complete drying out of the western basin of the Big Aral Sea occurred, and the composition of the remaining 9% of the brine of the ZGVCBAM changed greatly, which necessitated the study of its density, refractive indices and crystallization depending on temperature and salinity throughout the year.

The freezing point of the Aral Sea water at a salinity of 10-180 g / kg was determined depending on the cooling temperature of the samples taken from the surface of the ZGVChBAM during 2018 (Fig. 2).

The figure shows that with an increase in salinity, the freezing point of the samples decreases in a straight line from 0 ° C to -12 ° C.

Linear regression in the range under consideration gives an approximate formula: t = 0.0375 S1.1294 by salt meter and t = 0.0313 S1.1822 by titer. Based on the obtained experimental data and analysis of the reciprocal system $2Na^{+}$, Mg^{2+} // $2Cl^{-}$, SO_4^{2-}, H_2O, the following sequence of salt crystallization from the brine of the Aral Sea was established: $CaSO_4 \cdot 2H_2O$, NaCl, Na_2SO_4, $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$, $MgSO_4 \cdot 7H_2O$.

The resulting sum of density data was approximated by a quadratic form in temperature and salinity, the coefficients of which were selected by minimizing the standard deviation of the measured density values from the calculated ones.

As a result of these measurements, it was possible to draw up empirical equations of state for the ZGVChBAM brine in the following form:

а) $\sigma = A\, t^{b} S^{c} = 0{,}3122 t^{0{,}606} S^{1{,}1394}$

б) $\sigma = A t^{b} S^{c} = 0{,}2921 t^{0{,}606} S^{1{,}1710}$,

where, σ is the density, kg / m^3 (in the sense accepted in oceanology; the sample is reduced to atmospheric pressure at constant temperature and 1000 kg / m^3 is subtracted from the total density); t is temperature, ° C; S - salinity, g / l; A, b, c - coefficients.

During the expedition on June 15-25, 2014, soil samples were studied in the western basin of the Big Aral from sections from 45 ° 30 'to 44 ° 30' N. the western coast from a depth of 20-360 cm.

As the analysis of the samples shows, there are almost no carbonates in the salt rocks, since the content of HCO_3 and CO_2 in the samples did not exceed 0.02-0.078 and 0.002-0.009%, respectively. This is probably due to the fact that, under conditions of increased salinity, carbonates precipitate at the early stages of water salinity. The relatively high content of magnesium Mg / Na 17-21% indicates the presence of magnesium minerals in the samples: bleedite, konyaite, leveite and vanthoffite. Bledite and leveite are more common in the samples of the eastern coast from the ZGVChBAM, where irregularly shaped crystalline aggregates up to 854 μm in size are formed (transparent, glassy minerals covered with clay crystals ranging in size from 1 to 5 μm).

The regularity of distribution of clay materials and soluble soil salts was established, while the stratum of the western coast of the Great Aral Sea was divided into three layers: the first - 20 cm (from 0 to 20 cm); the second - 100 cm (from 20 to 120 cm); the third is 240 cm from (120 to 360 cm). In the first layer, there is no pattern of changes in the observed indicators. The second and third layers separately and the relationship have certain patterns. It was found that in the second layer, with increasing depth, the content of clay constituents of soils decreases, and at the beginning of the third layer increases again, but less than at the beginning of the second layer. These phenomena affect the nature of the distribution of soluble salts. It was established by chemical and physicochemical methods of soil investigation that the samples contain the following water-soluble minerals: mirabilite, thenardite, halite, bledite, konyaite, leveite, vanthoffite, pentahydrate, starkeyite, sanderite and kieserite.

A significant amount of salts falls out due to salt and dust storms (05/27/18). The center of the source of the Nukus storm had coordinates N-44°45, E-59 ° 15 with radii of 70 km, at an angle of the sector α-90 ° C with an expansion of the radius of propagation of more than 500 km towards the cities of Bukhara and Karshi, the amount of settled dust, although it decreases, by in total exceeds a million tons. Such winds with a speed of 10-27 m / s in the period from April to October are observed 10-15 times a year (15 million tons), and for the volatilization of thenardite, a wind speed of 2-4 m / s is sufficient, which lasts for 7 months in a year (210 days). At normal wind speeds, 210x200000 = 42,000,000 tons of salt evaporates. According to our calculated data, 57 million tons of salt are carried away from the Aral Sea annually.

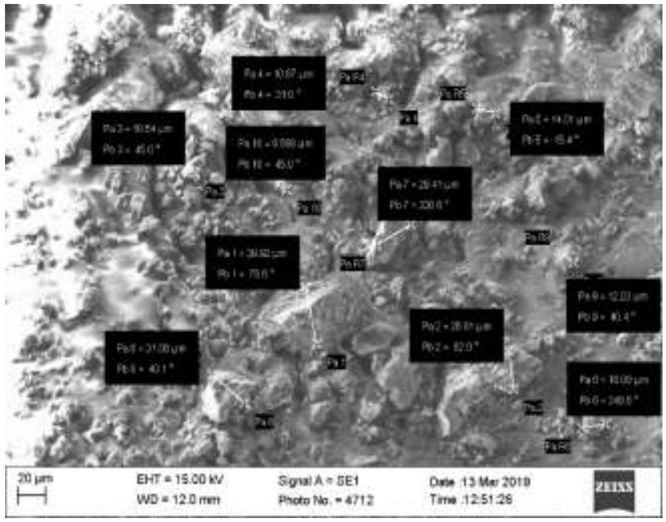

Figure 3: Images of microscopic particles and determination of their transverse dimensions

It can be seen from the photograph (Fig. 3) and micrographs that the sample consists of nano-particles with dimensions not exceeding 39.92 µm. Sample color is white with gray tints.

According to the analysis data, the samples taken from the salt dust of Nukus contain Na^{+}; Ca^{2+}; Mg^{2+}; SO_4^{2-}; Cl^{-}; CO_3^{2-}- ions, which mainly consist of sodium sulfate salts, since the ratio $\frac{SO4}{CL}$; $\frac{Na}{\Sigma(Ca,Mg,K)}$ equal to 22.04; 11.5.

The X-ray diffraction pattern of the sample (Fig. 4) clearly shows the diffraction bands with the values: 2.6542.791; 3.358; 4.303 Å, typical for Na_2SO_4; 7.670 Å ($CaSO_4 \cdot 2H_2O$); ($CaCO_3$); 2.828 Å (NaCl).

According to the desiccation and toxicological effect, these salts are divided into three classes: harmless - Ca $(HCO_3)_2$, $CaSO_4$, less harmful - Na_2SO_4, NaCl, $NaHCO_3$, $CaCl_2$, and harmful - $MgSO_4$, $MgCl_2$, Na_2CO_3.

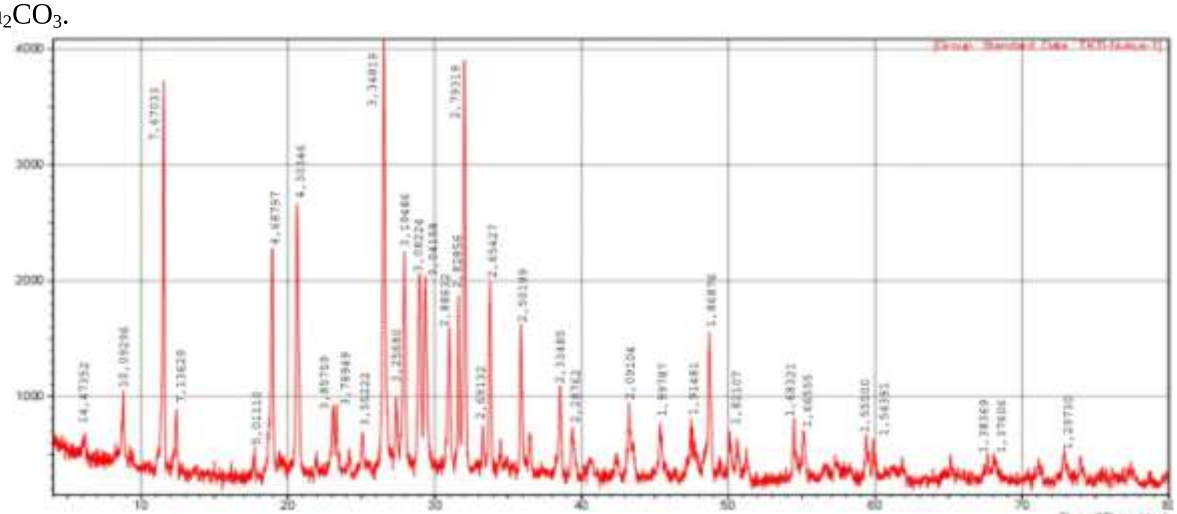

Figure 4: X-ray diffraction pattern of settled dust in the city of Nukus from the aerosol of the Aral Sea (May 27, 2018)

From the above, it follows that the process of draining the bottom of the Aral Sea has three zones of salt volatility, which are determined by the areas of gradual salt formation (Fig. 5).

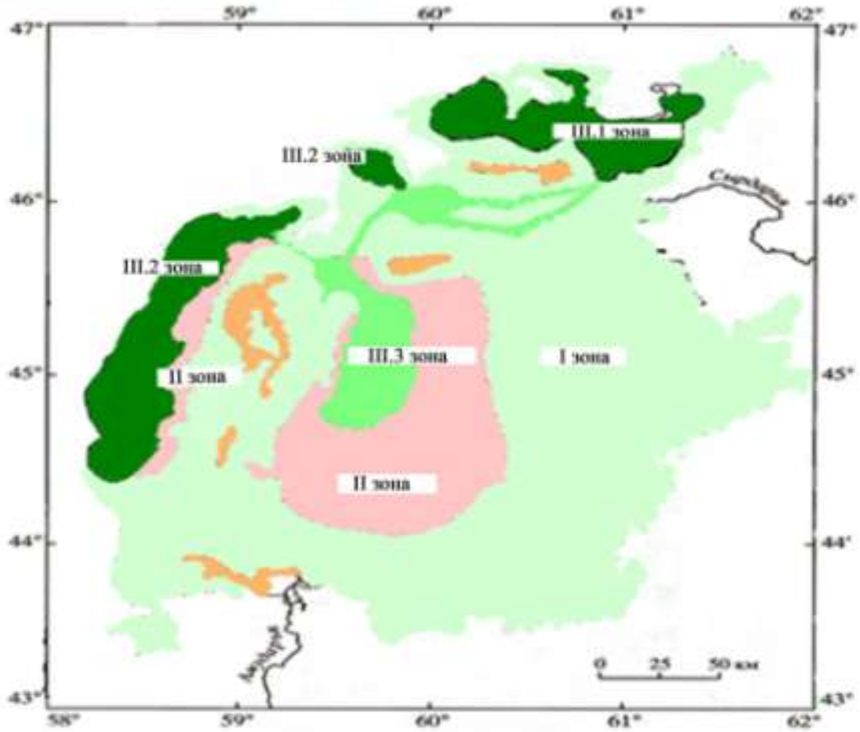

Figure 5: Boundaries of the Aral sea dry surface zone

In the first zone, the salt composition of groundwater changed from sulfate-chloride to chloride-sulfate with a predominance of chloride salts, and the amount of volatile salts was practically balanced. They are to some extent covered with salt and drought-resistant plants.

The second zone is the most terrible highly agitated salt source zone, since the remaining salts are sufficient (3119.548 - 62.39 · 20 = 1871.75 million tons) for more than 100 years, even for the annual carryover by a dust storm on average 18.71 million tons. tons of salts from the eastern basin of the Big Aral.

The third zone is more free from salt volatility. This is due to the fact that one part of the salt is in the form of a continuous layer of crystals with a thickness of (III-3) 2-48 cm, and the second part is covered with liquid brine 0.5-32.5 m deep, 0.01-1.0 m and water (III-1). Thus, simultaneously with the search for ways to improve the state of the Aral Sea, it is necessary to take measures to prevent salt loss, which is already causing great environmental and economic damage not only to the Aral Sea region, but also to the Eurasian region.

In our opinion, first of all, it is necessary to carry out the following measures: to fix the salt fluff on the territory of the second zone using various salt fixers; build a collector in a direction from south to north, so that groundwater flows from the second zone to the third; plant salt and heat-resistant plants in areas with low salinity; to organize the flow of brine from the third zone of the eastern to the western basin of the Big Aral.

Based on the foregoing, the main component of the salt dust of the Aral Sea is the low-harm thenardite Na_2SO_4. Therefore, the next task was to study the possibility of obtaining a fixative based on the reaction of formation of low-volatile salts NaCl and $CaSO_4 \cdot 2H_2O$ with the use of soda production waste - a distiller liquid, to determine the composition of the fixer films of saline soils of the drained bottom of the Aral Sea.

CONCLUSION

Based on the studies carried out with the establishment of regularities in the distribution of clay materials and soluble salts in the soil, the strata of the western coast of the Great Aral Sea was divided into three layers: the first 20 cm - (from 0 to 20 cm); the second 100cm - (from 20 to 120 cm); third 240cm - (from 120 to 360 cm). In the first layer, there is no pattern of changes in the observed indicators. In the second and third layers, separately and interconnected, there are certain patterns. It was found that in the second layer, with increasing depth, the content of clay components of the soil decreases, and at the beginning of the third layer increases again, but not less than at the beginning of the second layer. These phenomena affect the distribution of soluble salts. Chemical and physicochemical methods of studying water-soluble salts and water-insoluble soil residues have shown that the samples contain the following water-soluble minerals: mirabilite, thenardite, halite, bledite, konyavite, leveite, vanthoffite, pentahydrate, starkeyite, sanderite, and kieserite.

Based on the study of the chemical and mineralogical composition of the soil of the drained bottom of the Aral Sea and the dust settled in the city of Nukus from a salt-air storm, it was found that the main part of the salt components consists of monoparticles of volatile thenardite (Na_2SO_4). It is necessary to carry out the following measures: to fix the salt fluff on the territory of the second zone using various salt fixers; build a collector in a direction from south to north, so that groundwater flows from the second zone to the third; plant salt and heat-resistant plants in areas with low salinity; to organize the flow of brine from the third zone of the eastern to the western basin of the Big Aral.

REFERENCES

Cretaux JF, Kouraev AV, Papa *et al.*, (2005). Water balance of the Big Aral Sea from satellite remote sesing and in situ onservations, *Journal of Great Lakes Research* **31** (4) 520 - 534.

Erkaev AU, Reimov KD, Toirov ZK, Kaipbergenov AT, Turemuratova Ash (2014) Salt deposits and the current ecological state of the Aral Sea, *Uzbek Chemical Journal* **5** 4-20.

Erkaev AU, Reymov KD, Kaipbergenov AT, Ulashova NA (2016). Mineral composition of precipitation coas twestern large Aral Sea. *Austrian Journal of Technical and Natural Sciences*, **5-6** 63-71.

Erkaev AU, Yakubov RYa, Reimov *et al.*, (2019). Composition for fixing saline soils, Registered in the state, Patent No. IAP 05819. Register of inventions of the RUz.

Friedrich J, Oberhansli H (2004). Hydrochemical properties of the Aral Sea water in summer 2002, *Marine Systems*, **47** 77-88.

Goldstein GI, Newbury DE, Echlin P, Joy DC, Fiori C, Lifshin E (1981). Scanning electron microscopy and X-ray microanalysis, **New York: Plenum Press.** ISBN 0-306-40768-X.

Kurbanbaev E, Artykov O, Kurbanbaev S (2011). The Aral Sea and water policy in the republics of Central Asia, *Publishing house "Karakalpakstan"*, 128.

Lyman CE, Goldstein JI, Williams DB, Ackland DW, Vonharrach S, Nicholls AW, Statham PJ (1994) High-Performance X-Ray-Detection in a new analytical Electron-Microscope, *Journal Of Microscopy-Oxford*, **176** (2) 85- 98.

Pavia L, Gary M, Lampman George S, Kritz Randall G, Engel (2006). Introduction to Organic Laboratory Techniques, *Thomson Brooks/Cole*. 797-817. ISBN 978-0-495-28069-9.

Rubanov IV, Ishniyazov DP, Baskakova MA, Chistyakov PA (1987). Geology of the Aral Sea, *Tashkent: Fan*, 246.

Skoog DA, West DM, Holler FJ (1996). Fundamentals of Analytical Chemistry. 7th. ed. *Saunders College Publishing, Fort Worth*. ISBN 0-03-005938-0

Small EE, Giorgi F, Sloan LC, Hostetler S (2001). The effects of desiccation and climate change on the hydrology of the Aral Sea. *Climate.* **V** 14 300-322.
Vasiliev VP (1989). Analytical chemistry. Part 1. Gravimetric and titrimetric methods of analysis. *Higher School*, 320.
Zavialov PO, Ni AA, Ishniyazov DP (2008). Ongoing changes in salt composition and dissolved gases in the Aral Sea, *Aquatic Geochemistry*, doi. 2008.10.1007 / s 10498 - 008 - 905 - 79.
Zavialov PO, Ni AA, Kudyshkin TV (2008). Five years of field hydrographic research in the Large Aral Sea (2002 - 2006) *Journal of Marine Systems*, (in print).
Zavyalov PO, Arashkevich EG, Bastida *et al.*, (2012). The Big Aral Sea at the beginning of the XX century! century: physics, biology, chemistry, Institute of Oceanology named after P.P. Shirshov, Russian Academy of Sciences, Moscow: Nauka, 229.
www.Cawater.info / index. htm. Aral Sea database: G.N. Trofimov: Paleoclimatic situation, flow of ancient rivers and water balance of the Aral Sea in the Late Pleistocene and Holocene.