Hydrochemistry Comparison Research of Intercrystalline with Pore Bine and Pre-3D modelling of Heibeiwadi in Qaidam Basin

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Abstract. Intercrystalline and pore brine develop extensively in the Heibewadi research area which is located at south foot of Altun mountain of Qaidam basin. In central area, intercrystalline brine's depths range from 5m to 90m. In northwest, south area and central deeper area, pore brine develops under intercrystalline brine layer. The 2 types of aquifers have strong yield property, TDS is 200-350g/l with average of 276g/l. Main salt compound can be mined out economically. According to analysis result of intercrystalline brine, TDS, Cl^-, Na^+, K^+, Mg^{2+}, Li^+ irons'grades are very steady. That mean intercrystalline brine exist in the water-salt system under balance. Only thestability of Ca^{2+} and SO_4^{2-} are slightly poor. According the Kurtosis characteristics analysis, Ca^{2+}, SO_4^{2-} are no-normal positively platykurtic distribution, K^+,Cl^- and PH are normal positively platykurtic distribution. These 2 groups fall into a sub-class. And the combined with normal negatively platykurtic distribution-TDS and fall into platykurtic distribution group. Mg^{2+}, Li^+ are normal positively peaked distribution; Na^+ is normal negatively peaked distribution. They all belong to peaked distribution group. According to Na^+, K^+, Mg^{2+}//Cl^-H_2O quarternary phase diagram and Na^+, K^+, Mg^{2+}//$Cl^-SO_4^{2-}$H2O pentabasic phase diagram, the chlorite and magnesium sulfate subtype have different hydro chemical characteristics and salting-in and salting-out rules.

Introduction

Study area is located at northwest of the Qaidam Basin, an alluvial fan areas of south margin of Altun mountain. The main occurrence underground brine is confined brine with high TDS, K+ content is 0.55-11.28g/l, Na+ content is 27.62-107.42g/L. Main salt compounds with high economic values are KCl and NaCl. In recent years, various experts and scholars had completed independent research for widely distributed intercrystalline and pore confined brine based on exploration results in this area. Qindai Qaidam comprehensive geology exploration institute designed and finished detailed exploration for Heibewadi deposit area with spacing of 4km×2km and revealed more information of intercrystalline and pore brine in local area. Based on it, this paper is mainly focused on analyzing intercrystalline and pore confined brine water chemistry, phase diagram, geologic origin, modeling etc., and compare 2 types of underground brine, and it has important guiding significance for prospecting of potash and resource development.

Geological Research Background

Study area Heibeiwadi deposit is located at Saishiteng Mountain – Zongwulong mountain fracture which is connected to South Qilian faults system in western of Qaidam Basin, is Adjacent to Altun fracture and Tarim basin in Northwest direction and connected to Kunbei fracture and Kunlun orogenic belt in Southe direction.

From the old to the new strata exposed include Sinian, Ordovician, Devonian, Permian, Jurassic, Cretaceous, Tertiary and Quaternary in the region. Within the scope of Heibeiwadi Quaternary strata distributed widely. And the Quaternary strata distributed in sedimentary concave and valley areas near the foot of Altun Mountain. All strata from the Pleistocene to Holocene are exposed, and the geological origin type is complex, consist of Alluvial, Lacustrine, Aeolian and Chemical deposition.

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Deposits Distribution

In study area, all the underground high TDS waters which exist in halite crystals of halite, polyhalite, mirabilite and other chemical deposition layers and later tectonic fissures are called intercrystalline brine. And all the underground high TDS waters which exist in loose gravel pore are called pore brine. Intercrystalline brine distributed in the Holocene dabsan group, the Pleistocene Chaerhan group, middle Pleistocene Gaskule group, Holocene dabsan group and the Pleistocene Chaerhan groups and almost covers the Heibewadi area.

Intercrystalline brine occurs in chemical sediment layers and pore brine occurs in sandy gravel layers. Intercrystalline brine hollows widely distributed in the central area, the pore brine concealed in the lower area, deeper position in the middle area and relative shallower in the NW and SE areas. From West of Aqidam basin Liangzhong concave to Heibeiwadi concave and Chahansila concave, they composed a narrow space connected and similar structure regional concave. The upper areas of the concave are covered by chemical sediment layers and clay layers, lower areas are gravel layers. Chemical sediment layers contain confined intercrystalline brine while gravel layers contain confined pore brine.

Sampling and Analysis

Liquid samples of this study come from 2008 – 2012 drilled outer deep holes brine samples and 2013 -2014 regional general exploration stage drill holes brines samples.

Sampling method: During pumping test in each bore hole aquifer, after the water level become stable an liquid samples were taken for every 4 hours. Sampling bottles are new bottles which have been washed by distilled water. Promptly after the sampling, the bottles were sealed tightly with wax, labeled cemented by wide transparent tape and the sampling volume is generally 1,000ml.

After the water sample bottle wax seal opened, the PH value and fluid density were firstly tested, then draw 25mml diluted to 250mml and pour to a flask, and then draw 25mml from the flask and diluted to 250mml for analysis. Major ion analysis methods are as follows: K^+, Na^+, Li^+, Sr^{2+}, Rb^+, Cs^+ were tested by atomic absorption spectrometry; Ca2 +, Mg2 + were tested by EDTA volumetric method; Cl- were tested by $AgNO_3$ volumetric method; B_2O_3, HCO^{3-}, CO_3^{2-} were tested by acid-alkeli titration; SO_4^{2-} was tested by $BaSO_4$ gravimetric method ; Br, I were tested by spectrophotometry; PH was tested by ion electrode method; density was tested by the volumetric weighing method; TDS was tested by 105^{o} C dry weight method. Qinghai province Qaidam comprehensive geology institute laboratory undertook all the assay work.

Ion Content Characteristics

In constant ions, K^+ ion content is 0.55-11.28g/l. According to brine industry standards (cut-off grade is 0.3% KCl, industrial grade is 0.5%) After conversion, K+ cut-off grade is 1.98g / l, industrial grade is 3.28g/l. According to this standard, five drill holes (ZK2808, ZK4012, etc.) K+ content is lower than the cutoff grade; 11 drill hole (ZK3612, ZK4806, etc.) K+ is higher than the industrial grade; ion content of other 7 holes are between cut-off and industrial grade; all samples have an average grade of 4.68g/l. K+ ion content distributed in two relatively high areas, located near the 36 line and 48 lines. Na+ ion content is 27.62-107.42g/l, most more than industrial grade. Ca^{2+} ion content is 0.24-10.09g/l, at a relatively low level. Mg^{2+} ion content is 1.93-25.86g/l, the central region of the study area is slightly higher than the 2 ends.

Cl- ion content is 64.99-326.77g/l, except ZK4003 Cl- ion content is relative high as 326.77 g/l, the Cl- ion content of all other holes are 100-200g/l.

SO_4^{2-} ion content is 1.37-31.81g / l, part of holes have the higher levels of ion. The SO_4^{2-} ion is an important factor in the transition effects of brine hydro chemical type from chloride brine water chemistry type to magnesium sulfate subtype.

TDS is 106.55-342.2g/l, with an average of 276.06g/l, mostly more than 250g/l.

Based on comprehensive analysis, among 23 drill holes brine samples, 8 drill holes brine are chloride type and 15 drill holes brine is magnesium sulfate subtype.

Ions distribution

In order to describe the confined brine distribution rule in the study area, 5 liquid multiple tested samples whose hydro chemical types are magnesium sulfate subtype and distributed evenly (ZK3608, ZK4008, ZK4408, ZK4808, ZK5206) were analyzed for the study. Because of various factors, Salt Lake Brine elements (ion phase in the brine) content distributions are different; we use uniformity and normal distribution verification methods to measure their distribution rule. In order to research the distribution uniformity, in the paper we used variable coefficient of mathematical statistics as an indicator:

$$Ex = \frac{1}{n}\sum_{i=1}^{n} xi, \tag{1}$$

$$S = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(xi - Ex)^2} \tag{2}$$

$$Cv = \frac{S}{Ex} \tag{3}$$

In formula (1), Ex indicate average and xi indicate sample grade; in formula (2), S indicate deviation and in formula (3), Cv indicate variable coefficient.

Whether the elements follow normal distribution is one of the main characteristics of the element distribution. The mathematical statistics method - skewness, kurtosis test method can be used to determine the concentration of the various components of the frequency distribution histograms as well as the approximate frequency distribution function curve, and then determine whether the distribution of elements in brine follow normal distribution rule.

$$Cs = \frac{\sum_{i=1}^{n}(xi - Ex)^3}{nS^3} \tag{4}$$

$$Ce = \frac{\sum_{i=1}^{n}(xi - Ex)^4}{nS^4} - 3 \tag{5}$$

In formula (4) (5), $Cs < 0$ negative deviation, $Cs > 0$ positive deviation, $Ce < 0$ platykurtic kurtosis, $Ce > 0$ peaked kurtosis. Cs， Ce fluctuate within a certain range, that is considered to be normal distribution. Variogram, coefficient of variation and kurtosis coefficients for study area magnesium sulfate subtype brine samples were listed in the below table:

Table 1 Magnesium sulfate subtype brine distribution summary table

Items	Cv	Cs	Ce	Type
K^+ (g/l)	0.18	0.39	-2.71	Normal Positively Platykurtic Distribution
Na^+ (g/l)	0.08	-0.31	1.42	Normal Negatively Peaked Distribution
Ca^{2+} (g/l)	0.53	0.3	-0.97	No-normal Positively Platykurtic Distribution
Mg^{2+} (g/l)	0.36	1.23	0.84	Normal Positively Peaked Distribution
Li^+ (mg/l)	0.29	1.74	3.33	Normal Positively Peaked Distribution
Cl^- (g/l)	0.04	0.05	-1.69	Normal Positively Platykurtic Distribution
SO_4^{2-} (g/l)	0.7	0.62	-2.98	No-normal Positively Platykurtic Distribution
Density (g/cm^3)	0.01	0.15	2.01	Normal Positively Peaked Distribution
PH	0.03	0.56	-3.15	Normal Positively Platykurtic Distribution
TDS (g/l)	0.05	-0.22	-0.96	Normal Negatively Platykurtic Distribution

Note:Part of brine samples（B_2O_3，CO_3^{2-}，HCO_3^-not tested），not involved in the distribution analysis.

TDS, Cl^-, Na^+ and K^+ ions' Cv values are very low, indicating that their concentration in the brine are very stable with limited variation extent and evenly distributed; Mg^{2+}, Li^+ Cv values are slightly larger, but remain between 0 - 0.5, are relative stable components and relatively evenly distributed; Ca^{2+} and SO_4^{2-} ions' Cv values are between 0.5 -1, it is the relative unstable components, the distribution of the grade in the brine should be further analyzed and controlled; no component Cv values are greater than 1 with great floating. Brine components are generally stable.

The data were analyzed according to the ecological characteristics of regional ingredients, Ca^{2+}, SO_4^{2-} show no-normal positively platykurtic distribution, K^+, Cl^-, and PH show normal positively platykurtic distribution, these two groups can be further aggregated into positive platykurtic distribution, further combined with normality negative platykurtic distribution of TDS to aggregate into platykurtic distribution group. Mg^{2+}, Li^+ and density show normal positively peaked distribution, and combined with normal negatively peaked distribution of Na^+ to aggregate into peaked distribution group.

Phase diagram analysis and salting-out rule

Brines hydro chemical type depends on its major cations Na^+, Mg^{2+}, Ca^{2+}, K^+, and major anions Cl^-, SO_4^{2-}, CO_3^{2-} and HCO_3^- concentration and interaction. A different type of brine hydro chemistry type has a corresponding main ion composition and water - salt balance system. According to the main chemical analysis of the brine composition, it can be seen chloride type brine's major ion balance system is the Na^+, K^+, Mg^{2+} // Cl^-H_2O quaternary system, magnesium sulfate subtype brine's major ion balance system is the Na^+, K^+, Mg^{2+} / / $Cl^-SO_4^{2-}H_2O$ pentabasic system.

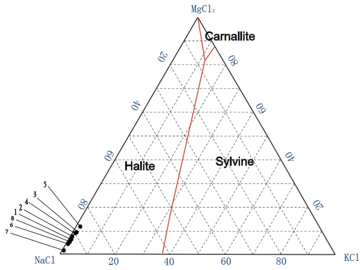

Figure 1 Na^+, K^+, Mg^{2+}//Cl^-H_2O (25ºC) quarternary phase diagram

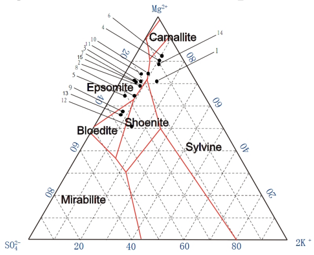

Figure 2 Na^+, K^+, Mg^{2+}//$Cl^-SO_4^{2-}$H2O pentabasic phase diagram

Because chloride brine containing low SO42- ion type, mainly precipitated compounds are NaCl, KCl, and $MgCl_2$. Brine samples of magnesium sulfate subtype are widely distributed in the bloedite, epsomite, Shoenite and sylvite area. It indicates that in magnesium sulfate subtype intercrystalline confined brine layers; there are some sub – aquifer that has similar structure and different chemical components proportion. Brine is mainly filled in the gap between Salt Lake deposit salt layers; mostly of the brine have high concentration. Between the various sub-layers there are some water-resisting layers with certain ability of penetration. On the one hand these water-resisting layers undertake the materials transportation works; on the other hand they can adjust the chemical balance between 2 sub-aquifers. Finally proportions of each sub - aquifers are close but still different. This can be also considered as one reason to explain the extensive distribution of magnesium sulfate subtype brine.

Brine occurrence structural modelling

Study area is close to south edge of Altun Mountain, located at a concealed huge alluvial fan base which extend by length of greater than 100km, width of 8-10km, partial thickness is greater than 800m. Heibeiaodi area is part of Dalangtan concave, located in the structures of No.1 Hongshanhan, Jiandingshan, Heiliangzi and Changweiliang. Because ii is impacted by Jiandingshan North insidious geology structure, the geology shape is irregular and looks as a long stripped shaped valley. The intercrystalline brines are distributed at central shallow area and pore brines gradually become thicker from central to 2 edges areas.

According to the exploration project constructed drill holes original logging data, total of 35 sub-halite and mirabilite layers were defined and 25 of them are sub-aquifers as well , halite content is

85% -90%, the phase is chemical sedimentary type. Since the pore brine widespread and no enough deep drilling could be undertaken to control it, the author is currently temporary created 25 intercrystalline brine layers by three-dimensional modeling using Surpac software. For those halite sub-aquifers which are only controlled by 1 or 2 holes, no models were created; models were only constructed for those more widely distributed halite sub-aquifer layers: 5, 7, 8, 18, 20, 21, 24, 25, 28, 29, 31, 33 ,a total of 12 brine layers solid were modelled to achieve the purpose of the regional quantify static brine capacity.

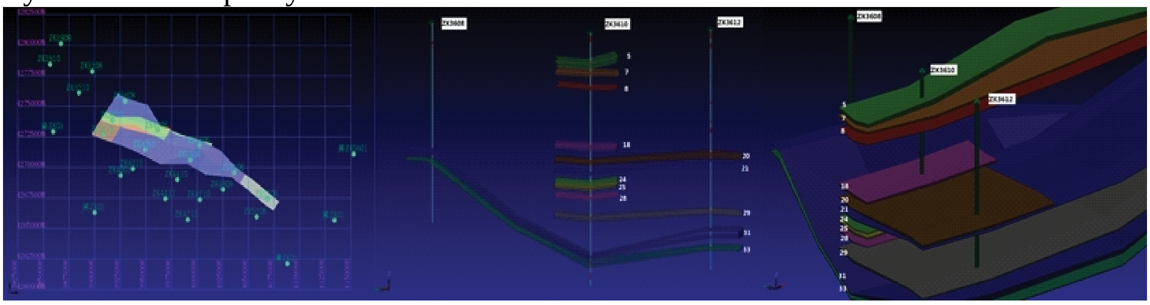

Figure 3 Three Dimensional models plan map, section map and long section map

According to preliminary estimation, in the study area the occurred static shallow crystal brine volume is about 20 million cubic meters, NaCl component content is about 5 million tons, MgCl2 is about 1 million tons, $MgSO_4$ 0.3 million tons, KCl 0.3 million tons. For pore brine, for there are not enough exploration data were collected, there is no modeling estimation. According to the data of the few deep drill holes, preliminary estimated potential resource number for pore brine aquifer is 30 million tons of NaCl, and 1.5 million tons of KCl. For groundwater dynamics research on influence of groundwater recharge rate and permeability coefficient to underground brine capacity, we need create further hydrogeological model to finish more accurate dynamic simulations. Actual mining dynamic resource will be much greater than the current estimated number than the amount of static resources.

Related Analysis

(1) According to the statistical analysis of the results of intercrystalline brine, TDS, Cl^-, Na^+, K^+, Mg^{2+}, Li^+ ions in the brine show stable concentration, low variation. It indicated that intercrystalline brine follow a certain equilibrium in water-salt system, the concentration of Ca^{2+} and SO_4^{2-} value stability is slightly worse, indicating that there are certain obstacles between sub-layers for the two ion transport with each other, or some exchange of material happened between intercrystalline and pore brines in some local areas.

(2) The final results of Table 2 shows, among the samples collected at this time, for magnesium sulfate subtype brine, sodium chlorine coefficient - C_{na} / C_{cl} values are 0.68-0.93; bromine chlorine coefficient values are 0.09-0.24, below than halite leaching brine (0.33); for chlorite type brine, sodium chloride coefficient C_{na} / C_{cl} values are 0.47-1.20; bromine chlorine coefficients values are 0.1-0.11, also lower than halite leaching brine (0.33).

When C_{na} / C_{cl} is 0.86-0.87 and $[Br^-]$ * 1000 / [Cl-] is 0.33, the brine is marine origin sedimentary brine; when C_{na} / C_{cl} value is 0.87-1.2 or higher and $[Br^-]$ * 1000 / $[Cl^-]$ value is 0.33 or less, the brine type is halite leaching brine, when C_{na} / C_{cl} value is less than 0.87 and $[Br^-]$ * 1000 / $[Cl^-]$ is greater than 0.33, the brine type is sedimentary metamorphic brine. $[Ca^{2+}]$ / $[Mg^{2+}]$ coefficient reflects the metamorphic degree of stratum brine, intercrystalline brine sample average values are 0.5 or less, the pore brine average values are 0.9. It shows the intercrystalline brine metamorphic degree is low for the brine main occurs in un-closed environment; $[Ca^{2+}]$ / $[Mg^{2+}]$ coefficient of pore brine is less than the average of the Qaidam Basin deep water value.

The reason may be due to the pore-forming time is relatively late, there is no enough time for completing the metamorphism.

Desulfurization coefficient 100 * $[SO_4^{2+}]$ / 2 $[Cl^-]$, the values are 0.17-1.73 for pore brine, and 0.3-3.16 for intergranular brine. Since pore brine experienced reduction of sulfate, so desulfurization coefficient isless than intercrystalline brine. For both intercrystalline and pore brines, brine desulfurization coefficients are less than experienced values (experienced value for intercrystalline brine is 10.67), the overall desulfurization effect is poor according to the data analysis

(3) According to three-dimensional model calculated resource, Heibewadi intercrystallinre brine deposit resource number is relatively small but easier for mining, although pore brine resource is larger but occurred at deeper elevation and not proper for current mining under low cost, in addition we still can consider the pore brine as long - term potential resource.

(4) Based on the analysis of the Na^+, K^+, Mg^{2+} // $C^{l-}H_2O$ quaternary system, Na^+, K^+, Mg^{2+} analysis // $Cl^-SO_4^{2-}H_2O$ quintuple system, majority of intergranular brine is sulfate magnesium subtype brine, pore brine is chlorine type. At the same time because of the local geological structure is abnormal, it leads to acceleration or substance of materials transportation, and there are also phenomenons that two types of brine chemistry conditions can convert into each other, which can explain exceptional intercrystalline or pore brine drill holes are located at opposite areas. Two brine chemical types intrinsically have certain relationship

Conclusion

In the Heibewandi research area of Western Qaidam Basin north edge of Altun Mountain, intercrystalline and pore brines are widely distributed. In central area, intercrystalline brine's depths range from 5m to 90m; In northwest, south area and central deeper area, pore brine develops under intercrystalline brine layer. The 2 types of aquifers have strong yield property, TDS is 200-350g/l with average of 276g/l. Main salt compound can be mined out economically by the order of intercrystalline brine to pore brine

According to statistical analysis of the results of intercrystalline brine, TDS, Cl^-, Na^+, K^+, Mg^{2+}, Li^+ ions in the brine concentration are stable. It indicated that intercrystalline brine follow a certain equilibrium in water-salt system, the concentration of Ca^{2+} and SO_4^{2-} value stability is slightly worse. According to analysis of constituents kurtosis characteristics in the study area, Ca^{2+}, SO_4^{2-} are non-normality positive platykurtic distribution, K^+, Cl^-, and PH are normal positive platykurtic distribution. These two groups can be further aggregated into positive low platykurtic distribution, further aggregate into platykurtic distribution with normal negative platykurtic distribution TDS. Mg^{2+}, Li^+ and density are normal positive peaked distribution, and can be aggregated into peaked group with normal negative peaked distribution Na^+

In the Na^+, K^+, Mg^{2+} // Cl^-H_2O quaternary system, Na^+, K^+, Mg^{2+} // $Cl^-SO_4^{2-}H_2O$ quintuple system phase diagram, the analysis result reflects the different salting law for chloride type brine and sulfate magnesium subtype brine.

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