

GEOCHEMISTRY OF HUASCO SALAR'S, CHILE. ORIGIN OF SOLUTES AND BRINE EVOLUTION

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The Salar of Huasco is a modern saline continental system located in the Andean region of the northeast of Chile. The extremely arid conditions, altitude, volcanic activity to result in a high evaporation rate, yielding brines of high ionic strength. This is of special importance considering that these lakes are located in a desert region rich in minerals with an increasing mining activity. The stratigraphic record of the salar basin shows a central massive saline crust (mirabilite 1 m thick), surrounded by an aureole of fine clay-saline material with a superficial saline crust of a few centimeters composed of chlorides and sulphates. All these deposits were generated in a paleolake developed during the late Tertiary. At present surface waters cover only a minor part of the salar surface.

A mineralogic analysis shows that the salar mainly formed by sulphate crusts (mirabilite, thenardite), with a substrate formed by fine saturated sediments with interstitial dissemination of crystals. Chlorides (halite) and sulphates, 20 cm thick form the central part (nucleus). The bottom part of the salar contains hydrated sodium sulphate (mirabilite) with crystals layers up to 1 cm thick.

The brines of Huasco salar's are $\text{Na}^+ > \text{SO}_4^{2-} > \text{Cl}^-$ type. The cationic composition is more homogeneous, with alkaline elements (sodium and potassium) always prevailing over calcium and magnesium.

The solutions are in equilibrium with calcite, reaching equilibrium with gypsum and mirabilite when the concentration increases. In the final stages the most concentrated brines are in equilibrium with halite, sylvite and syngenite. The quantities of mirabilite found in these salars is what makes them attractive for commercial exploitation, but the climate conditions are a problem.

1. THE SALAR OF HUASCO

Huasco Salar is a 70 km² closed basin located between 7725-7761 N and 512 E, at an altitude 3900 m. The deepest part of the basin is filled with alluvial sediments. Inflow is stems only from meteoritic waters precipitated at the high mountains and coming into the basin as surface waters or as underground waters. The salar is flooded during the summer season and dry the rest of the year. In the dry season the subsurface brine evaporates by capillary draw through of the crust. Only one strip of the brine remains exposed all year, between 8-20 cm above the sediment at the western side.

Brine chemistry: The brines has density between 1.0 g/cc and 1.225 g/cc, which is proof of the high variability of the system. The temperature of these waters is low and they are slightly alkaline, with average pH 8.23 to 8.30.

The brines are classified, and contain mainly $\text{Na}^+ > \text{SO}_4^{2-} > \text{Cl}^-$, while $\text{K}^+ > \text{HCO}_3^- > \text{Ca}^{++} > \text{Mg}^{++}$ are in found in lower concentrations. The concentration of most of the solutes increases with increasing salinity. The relative concentrations of SO_4^{2-} and Na^+ increase with increasing ionic strength and the relative concentrations of Ca^{++} and CO_3^{2-} decrease with increasing ionic strength. The ionic ratio of SO_4^{2-} increases from more than 30% as equivalents,

while amount of K^+ is always less than 20% total cation amount and its ratio does not change as increasing salinity.

Mineralogy. The central zone is a massive saline nucleus with a white surface, and a maximum thickness about 1.5 m, consisting of halite and thenardite. From the center toward the north sector there also eugsterite and singenite are found. Different sulphates, carbonates and borates have been detected (hidroboracite, probertite and to a lesser extent (<5%) ulexite). The saline crust in north-west zone, is about 5 to 10 cm thick, gray-brown in color, shows irregular relief and variable porosity. Below this crust detritic-saline material, dark gray colour containing interstitial brine is found. The mineralogical composition of the crust is mainly gypsum, halite and thenardite. Minor minerals are sulphates (glaserite, polihalite), probertite and camalite. Samples from the saline-detritic sediments below that crusts are more varied in composition, from gypsum and halite and others materials detritics. The south-west area contains mainly halite, thenardite and gypsum. The north-east sector is characterized mainly by gypsum and quartz in the external shore but toward the center of the salar singenite, eugsterite and halite begin to appear. The minerals in central west area are gypsum, halite, singenite, eugsterite and thenardite, minor sulphates like loeweite, mirabilite and polihalite besides nitratina and probertite are also found. At the same

time the samples from underground sediments have high proportion of detritic minerals, gypsum and calcite. The south-east sector is similar in composition, containing halite, thenardite singenite and eugsterite.

3. DISCUSSION AND RESULTS

The climate of the Huasco salar basin is very dry. The principal inflow of water is on the NW and SE border of the basin. Rainfall occurs in summer. This unsymmetrical contribution of water causes a continuous circulation of the water over the surface of the salar from W to E, running almost only over the S border because a slight slope in the basin. This circulation causes a progressive evolution of the concentration of the solutions due to the strong evaporation and contact with saline substratum at the inner part of the salar.

The initial chemical composition of the waters (NW) is mainly carbonated, and markedly poor in alkaline terreous cations. These solutions upon reaching the salar progressively increase their concentration because of the strong evaporation. The chemical evolution of the solution is conditioned by certain elements ratio in the starting solution, mainly calcium and bicarbonate. The theoretical model of *Hardie and Eugster* (1), (2), developed for the evolution of the water can take two paths. If $(\text{alk}) > 2(\text{Ca})$, the solution become carbonate rich and calcium poor (facie alkaline, pH above 10) in this case leads to sequential precipitation of calcite, magnesium silicate, sodic carbonates and halite. The neutral way means, If $(\text{alk}) < 2(\text{Ca})$, then the pH remains below 9 and its evolution leads to the precipitation of calcite, gypsum, mirabilite, and halite. According to that our data the evolution of the solutions is along the neutral way.

The former disagreement between the theoretical evolution of the solutions and the actual data is due to the concentration process by interaction between the contribution waters and the saline crust. This crust acting by dissolution of the salts, gives the water similar chemical characters to that of the lake from which the saline deposits were formed. Dissolving of some gypsum at the sulphated saline zone increases the calcium concentration in the solutions. The ratio of the $([\text{HCO}_3^-] > 2 [\text{Ca}^{+2}])$, formerly favoring carbonates and going to an alkaline evolution, is reversed by the calcium contribution from gypsum dissolution thus directing the later evolution of the solutions along neutral way. Samples from the CE zone of the salt flat, in addition to the W zone solutions not corresponding to composition of the diluted contribution waters, shows a

value of the quotient $[\text{HCO}_3^-]/2*[\text{Ca}^{+2}]$ lower than unity. These solutions are clearly undersaturated in gypsum at the lower concentration steps before reaching the salar. Along its evolution marked by the increase in chloride concentration, the gypsum saturation index slowly increases in the input waters, as can be seen from the inner zones of the solution which are already in equilibrium with gypsum at similar conditions.

Physicochemical Evolution: The activity coefficient has been evaluated (3) by Pitzer's equation and thermodynamic equilibrium by means of the mineral saturation index. In all samples calcite and gypsum are very close to the equilibrium; there are many samples in equilibrium with mirabilite (in the central part). The concentration gradient towards the inside of the salar leads to progressive increasing of the mineral saturation index, and the solutions reach the equilibrium with halite and sylvite at ionic strength 8 molal. Some other very soluble salts like singenite, glauberite and glaserite are near to the equilibrium.

The evaporative concentration of the inflow waters leads neutral brines of the Na-Cl-(SO₄) type. This is in contradiction with the calculated evaporation path based on thermodynamic equilibrium, which indicates that inflow waters would be alkaline brines. The loss of alkaline is due probably to interaction between these solutions and the saline material of the system.

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