

MODELLING OF MULTI-COMPONENT SALT SOLUTION MINING

by

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SUMMARY

Billiton International Metals, a member of the Royal Dutch Shell Group of companies, is applying the solution mining technique to recover magnesium-chloride-containing brines from carnallitic deposits in the northern part of the Netherlands. These brines will be further processed to magnesium oxide.

As part of this project Billiton is sponsoring a research programme at the Koninklijke/Shell-Laboratorium, Amsterdam (KSLA). An extensive study has been made of the dissolution behaviour of multicomponent salts. On the basis of this investigation a theoretical model has been developed which describes the down-hole leaching process in ores containing carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$), halite (NaCl), bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$). The model has been checked against field data from an actual cavity; the calculated data show very good agreement with the measured results.

INTRODUCTION

Whilst exploring the gas field in the northern part of the Netherlands, the Shell Group discovered large magnesium-containing salt deposits at depths of 1500 - 2000 metres. The most interesting deposits were found in the third evaporative cycle of the Zechstein: mixed carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$), bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) and halite (NaCl), with a total height of over 100 metres in some places¹.

In the early 1970s, Billiton International Metals, a member of the Royal Dutch Shell Group of companies, investigated the feasibility of commercial exploitation of these Mg-containing deposits. Billiton decided to produce a refractory quality MgO using the Harbison and Walker technology; MgCl_2 obtained by solution mining of the Mg-bearing deposits, and burnt dolime ($\text{CaO} \cdot \text{MgO}$) would be used as the raw materials for this process.

In 1973 a few exploratory wells near Veendam were taken into operation to gain experience with the solution mining of carnallitic ore. A bottom injection/top production mode was applied; the resulting brine, however, was rather weak. At Billiton's request, the Shell laboratories at Amsterdam (KSLA) subsequently became involved in the project, to advise on the solution mining mode and to predict how the brine concentration would develop with time.

With respect to the first request, we advised Billiton to apply a top injection/bottom production mode; this resulted within a very short time in a commercially acceptable concentration of MgCl_2 in the brine.

To predict the development of brine concentration with time, we carried out an extensive investigation which comprised the following three elements:

- determination of the multicomponent phase equilibria;
- detailed modelling of the hydraulics in the cavity for the top injection/bottom production mode;
- determination of the dissolution rates of the different salt components in unsaturated brines.

The results of these studies were used to develop a computer program quantifying the time-dependent leaching behaviour of the multicomponent Veendam ore. With this computer program the cavity brine concentration and cavity growth have been calculated as a function of injection rate and ore composition. In the following sections the studies and the computer program are described in more detail.

THE MULTICOMPONENT PHASE EQUILIBRIA

For brines produced from ores containing halite, carnallite, bischofite and kieserite the phase equilibria of the quinary system $\text{MgCl}_2\text{-MgSO}_4\text{-KCl-NaCl-H}_2\text{O}$ must be known. As the phase equilibria of this system are very complex, we initially concentrated on the quaternary system $\text{MgCl}_2\text{-KCl-NaCl-H}_2\text{O}$, using the data of Autenrieth and Braune² and of D'Ans³.

The most important phenomenon for our process is the selective dissolution of carnallite. When carnallite is dissolved in water, the concentrations of KCl and MgCl_2 will develop as shown in Table I*. Two stages in the carnallite dissolution process can be distinguished:

- (i) non-selective dissolution, where the brine is not saturated with potassium chloride, followed by
- (ii) selective dissolution, where only MgCl_2 will dissolve, and previously dissolved KCl will precipitate.

Table II* shows the brine concentration development when carnallite is dissolved in a saturate solution of sodium chloride. The data show that in the presence of NaCl the selective leaching of MgCl_2 starts at lower KCl levels. When bischofite (a pure magnesium chloride salt) is also present in the ore the MgCl_2 concentration in the brine will increase to very high levels of 30 - 35 %w, and even more KCl and NaCl will precipitate.

As can be seen from Tables I and II, the higher the MgCl_2 content of the brine, the less the brine is contaminated with other components, and a relatively pure, concentrated MgCl_2 brine will be produced from the bottom of the cavity.

THE HYDRAULICS IN A CAVITY

To be able to describe the hydraulic flow in the cavity the following assumptions have been made:

- (1) The flow in the cavity is laminar.
- (2) The cavity operates isothermally.
- (3) There are no density differences in the cavity in any horizontal plane.
- (4) The vertical density gradient ($\Delta\rho/\Delta H$) in the cavity is positive in the downward direction.

Re (1): Water is injected in the Veendam cavities at a flow rate of 10 to 30 m^3/h ; since the diameter of the cavities is relatively large - as much as 100 metres - the linear velocity in the cavities will be very low and flow will be laminar.

* Data taken from refs. 3 and 4.

- Re (2): The Veendam cavities are not very deep (± 100 m); temperature differences between top and bottom due to the temperature gradient in the formation are thus very small. The injection of water at the top does not influence the temperature of the cavity because of the dual string completion used in the well which acts as an almost ideal heat exchanger with a length of 1500 - 2000 m.
- Re (3): Any density differences in a horizontal plane will be nullified by flow circulation in the cavity.
- Re (4): From the literature and experiments it appears that the density of MgCl_2 brines such as those produced from the Veendam cavities will increase somewhat with increasing MgCl_2 concentration in the brine. Therefore, the positive gradient of the MgCl_2 concentration profile in the cavity corresponds to a positive density gradient.

DISSOLUTION RATES OF THE DIFFERENT SALT COMPONENTS

The dissolution rates of the different salt components were determined experimentally. For this purpose pieces of halite, carnallite and bischofite were dissolved in water as well as in unsaturated brines of the quaternary system $\text{MgCl}_2\text{-KCl-NaCl-H}_2\text{O}$. To study the influence of temperature the experiments were carried out at 25 and 55 °C.

A unique relation was found between the dissolution rates of carnallite and bischofite and the total chloride concentration of the brines in which the salts dissolve: the dissolution rate decreases strongly with increasing chloride concentration (see Figures 1 and 2).

In addition to carnallite, bischofite and halite, the Veendam ore also contains minor amounts of kieserite. Although this material dissolves very slowly in water or brine (see Figure 1), the amount dissolved can be large, owing to the extremely small particle size and the natural distribution of the kieserite in the ore. The concentration of magnesium sulphate in the brine therefore cannot be neglected.

OPTIMUM ORE RECOVERY

From the results of the studies on phase equilibria, hydraulic flow in the cavity and dissolution rates, it can be seen that the dissolution process in the Veendam cavities is almost wholly concentrated at the top of the cavern. The shape of the cavity will therefore develop in the form of an inverted cone ("morning glory" shape), leaving a large proportion of ore unmined.

We have developed a mining procedure which improves ore recovery considerably whilst producing a brine with a high MgCl_2 concentration at the same time. In this procedure, the total body of ore is leached in a

series of many small salt cuts with a height of a few meters each. The roof of every new cut is protected against leaching by the injection of oil. When the leaching of a new cut is started, the dissolution process in the previous cut continues until, eventually, carnallite saturation is reached. At the end of this saturation process, the radius of the cavity has approached the mining limit of 50 meters.

DESCRIPTION OF THE COMPUTER MODEL

For the calculations it is assumed that the multicomponent ore is present in horizontal layers. The composition of these layers is derived from bore-hole loggings; dip angles and variations in ore grade are not taken into account. Further, the reverse flow circulation mode (i.e. top injection/bottom production) is assumed.

Each ore layer is subdivided in smaller computational cells with heights up to 1 meter. For each cell the model computes the mass of salts dissolved, the new cell radius, the brine composition and the mass of precipitating solids during a small time step, Δt . The calculation cycle starts at the bottom computational cell, from which brine is produced, and proceeds to the top cell, in which the fresh water is injected. By iteration, the development of cavity shape and cavity brine concentration with time, as a function of injection rate, cavity height and ore composition, can be calculated.

We have tested the model against practice by calculating the concentration development for the first three cuts of one of the Veendam wells (Ve-2) and comparing these results with point data measured at the well. As can be seen from Figure 3, the predicted data are very promising, and we intend to use the computer model to predict the performance of future production wells.

REFERENCES

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Table I

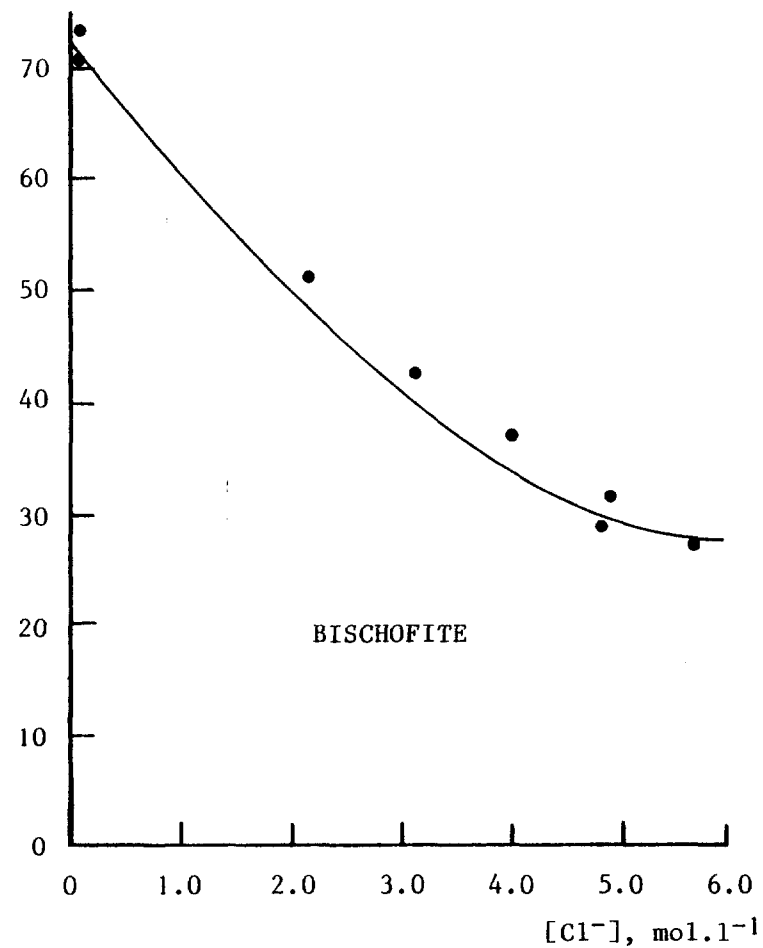
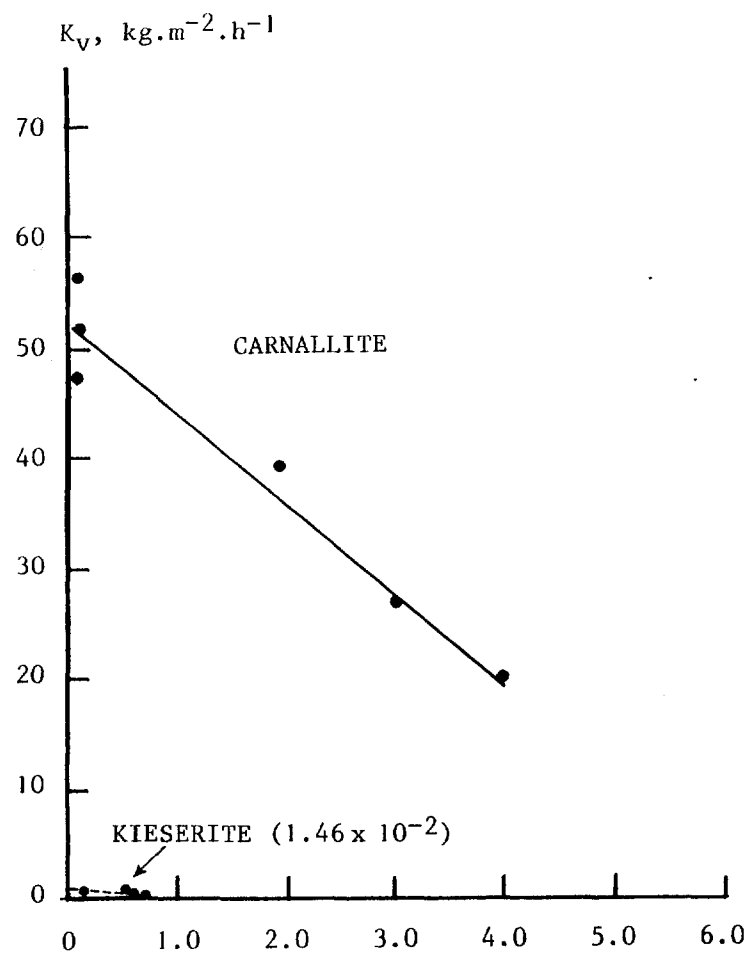
Development of MgCl_2 and KCl concentration during dissolution of carnallite in water

MgCl_2 , %w	KCl , %w	
0	0	Non-selective dissolution ↓
3.8	3.0	
8.6	6.8	
12.7	9.7	
14.7	11.5	
17.8	9.6	Selective dissolution; KCl precipitation ↓
20.5	7.7	
23.1	6.0	
25.7	4.5	
26.9	3.8	

Table II

Development of MgCl_2 , KCl and NaCl concentration during dissolution of carnallite in a saturate solution of sodium chloride

MgCl_2 , %w	KCl , %w	NaCl , %w	
0	0	26.8	Non-selective dissolution; NaCl precipitation ↓
4.0	3.1	20.7	
8.0	6.2	14.7	
11.2	8.7	10.4	
12.0	8.4	9.7	
16.0	7.0	6.8	Selective dissolution; KCl and NaCl precipitation ↓
20.0	5.7	4.6	
24.0	4.4	2.7	
26.4	3.5	1.6	



FIGURES 1 AND 2
DISSOLUTION RATES OF CARNALLITE AND BISCHOFITE AS A FUNCTION OF $[\text{Cl}^-]$

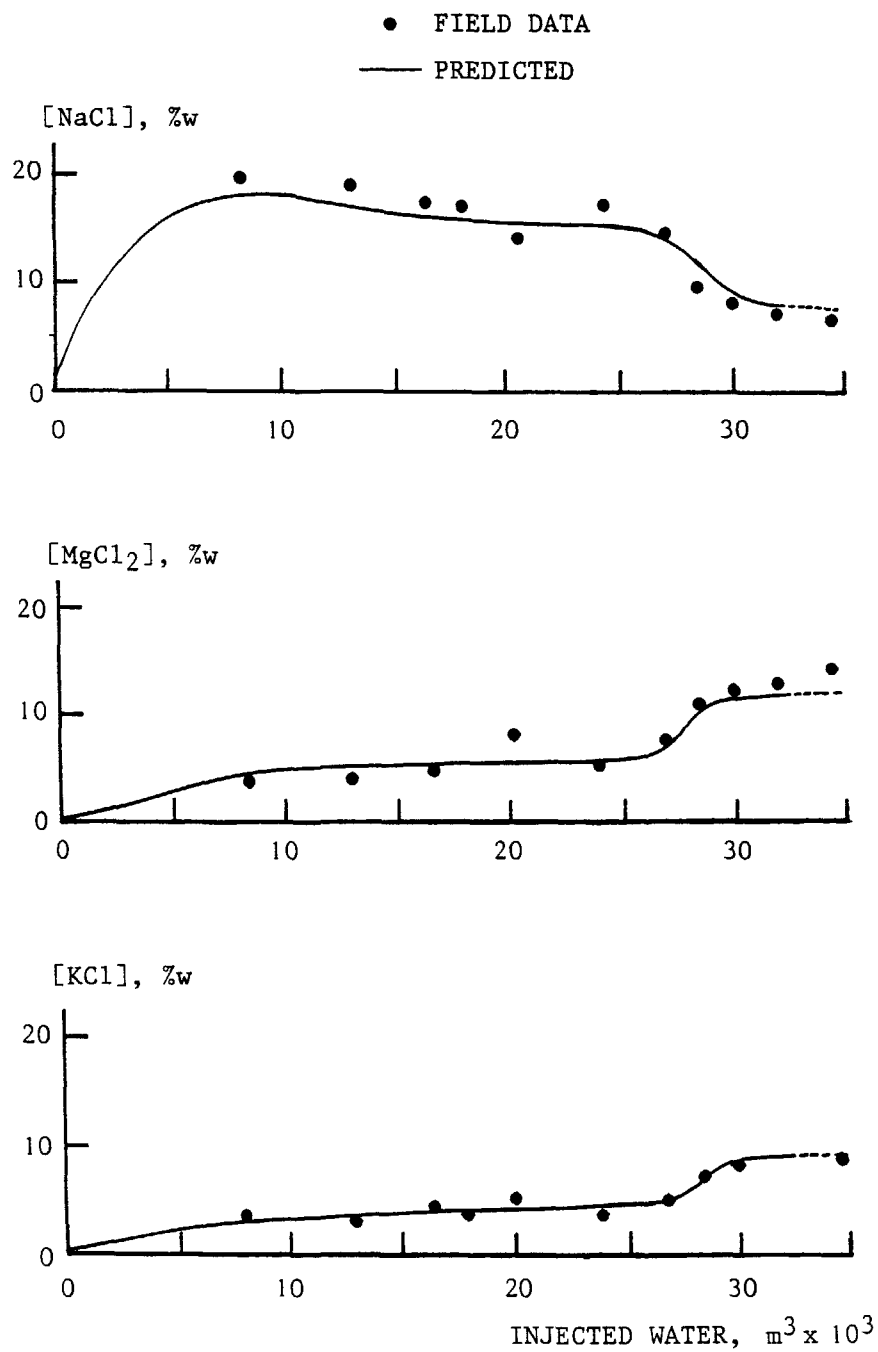


FIGURE 3
BRINE CONCENTRATION DEVELOPMENT vs INJECTED WATER VOLUME