Seventh Symposium on Salt, Vol. I 369–376 (1993)
Elsevier Science Publishers B.V., Amsterdam

Measurements of the Rates of Dissolution and the Petrography of Some Mixtures of Halite, Sylvite and Carnallite

A. Goor[1], I.J. Lin[2] and J. Metcalfe[1]

[1]*IMI (TAMI) Institute for R&D Ltd., P.O. Box 10140, Haifa Bay 26111, Israel*
[2]*Mineral Engineering Department, Technion, Haifa, Israel*

ABSTRACT

Artificial ore samples were prepared by mixing different ratios of sodium chloride (halite), potassium chloride (sylvite) and carnallite (potassium magnesium chloride) with similar size distributions and subjecting them to a compaction pressure. The porosity of the resulting samples was measured at different compacting pressures. It was found that the porosity approached a minimum value at a compacting pressure of about 6 t/cm^2 for mixtures containing carnallite at room temperature, and so samples for the dissolution rate experiments were prepared at this compaction pressure.

The spatial distribution of the potassium containing salts in the compacted samples was examined using the techniques of autoradiolysis and selective staining. The method of selective staining gave good results and is the preferred method as it is much faster than autoradiolysis.

The dissolution rates were measured on compacted samples using the method of Cofman (1931). A compacted sample, which was sealed in polyester resin such that only one face was exposed, was suspended from a balance in a dissolution brine and the rate of weight loss and therefore the dissolution rate were determined. Dissolution rates were measured at different temperatures, between 20 and 60°C, and at different brine compositions, between pure water and saturated salt solutions.

The dissolution rates of pure salts have previously been shown by Rohr et al. (1980) and Saberian (1981) to be dependent on the concentration of salts in the dissolution brine and on the temperature. The present work examines the effects of these parameters on the rate of dissolution of mixed salts.

This work is relevant to the process of solution mining of potassium salts as these salts usually occur mixed with sodium chloride.

INTRODUCTION

The rate of dissolution of pure salts in water under free convection can be calculated using the formula derived by Durie and Jessen (1964) and the theoretical values agree well with experimentally measured values until surface irregularities are formed. Saberian (1981) has reviewed the literature on potash dissolution (and partially on halite dissolution). This review presents extensive data on the effects of flow velocity, solute concentration, surface inclination, and temperature on the dissolution rates of potash and halite. The literature on the rates of dissolution of salts under conditions which will occur in a selective extraction processes, where one or more salt may be precipitating while other salts are dissolving, is much more limited, for example the papers by Taylor et al. (1967) and Walden et al. (1969).

The present study investigates the rates of solution of mixed ores of halite, sylvite and carnallite under both total dissolution and selective dissolution conditions.

Husband and Ozsahin (1967) have shown that natural ores are too variable to allow reproducible results to be obtained, so synthetic ores were prepared by compacting mixtures of halite, carnallite and sylvite in the required concentrations.

PREPARATION OF SAMPLES FOR THE DISSOLUTION TESTS

The halite, carnallite and sylvite used in preparation of the compacted samples (plugs) for the dissolution tests and the petrographic studies were commercial samples from the Dead Sea Works. The

TABLE 1

Chemical analysis of the raw materials for the salt plugs

Salt	% NaCl	% KCl	% $MgCl_2$	% Purity	% Insolubles
Halite	99.8	0.04	0.14	99.8	<0.05
Sylvite	12.0	84.1	0.38	84.1	<0.05
Carnallite	3.0	23.3	30.2	88	<0.05

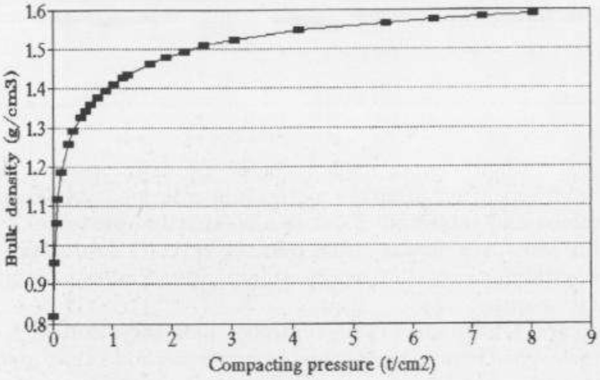

Fig. 1. Compaction curve for 88% carnallite.

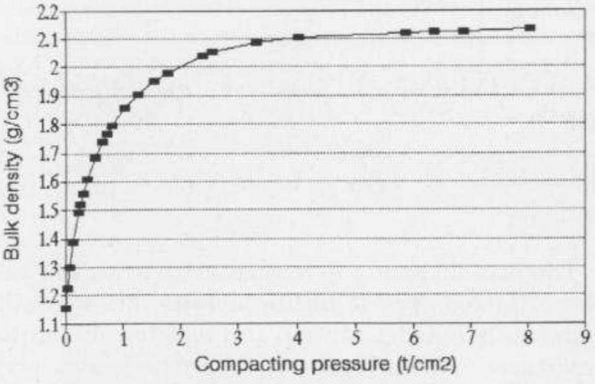

Fig. 2. Compaction curve for 100% halite.

samples were sieved to give a fraction between 0.60 and 2 mm. A chemical analysis of the sieved salts after drying is given in Table 1.

The table indicates that there is a problem obtaining dry carnallite either due to problems in drying (due to occluded brines) or due to the hygroscopicity of the salt.

Dissolution brines containing NaCl were prepared using halite from the same source. Salts found in salt beds usually have a very low porosity due to being subjected to high lithostatic pressures for long times and so the conditions under which low porosity plugs of salts could be formed in the laboratory were studied.

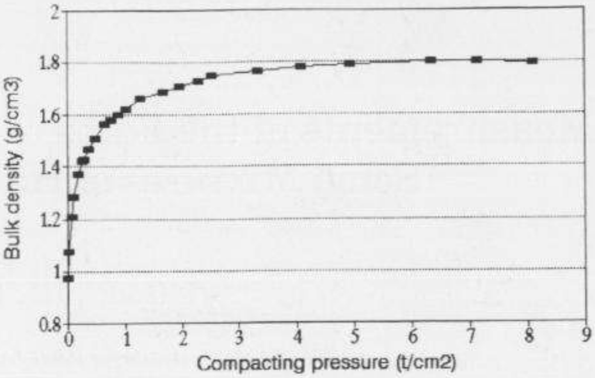

Fig. 3. Compaction curve for 45% halite/55% carnallite.

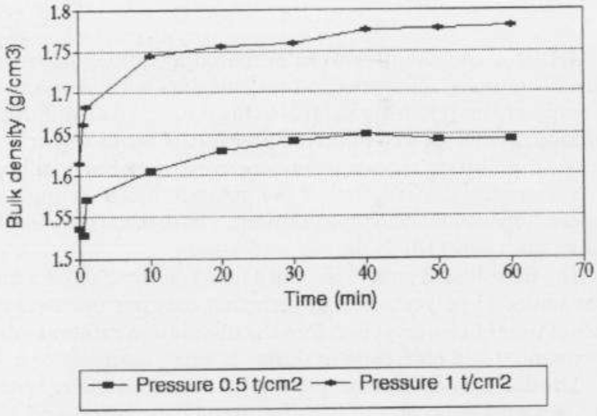

Fig. 4. Bulk density versus time for 45% halite/55% carnallite.

The effects of compaction pressure on the density of salt plugs, compressed for times of the order of seconds, were studied for samples of 88% carnallite, 100% halite, and 45% halite/55% carnallite as shown in Figs. 1–3. The change in density with time at a constant compacting pressure is shown in Fig. 4 for a mixture of 45% halite/55% carnallite.

These results show that salt plugs with low porosity can be formed either by compacting at a low pressure (1 t/cm^2) for a period of about 40 min or by using a higher compaction pressure, (6 t/cm^2), with compaction times of the order of seconds. (Metric tonnes are used throughout this report).

For convenience the plugs for the dissolution tests and the petrographic studies were prepared using a compaction pressure of 6 t/cm^2 with compaction times of a few seconds.

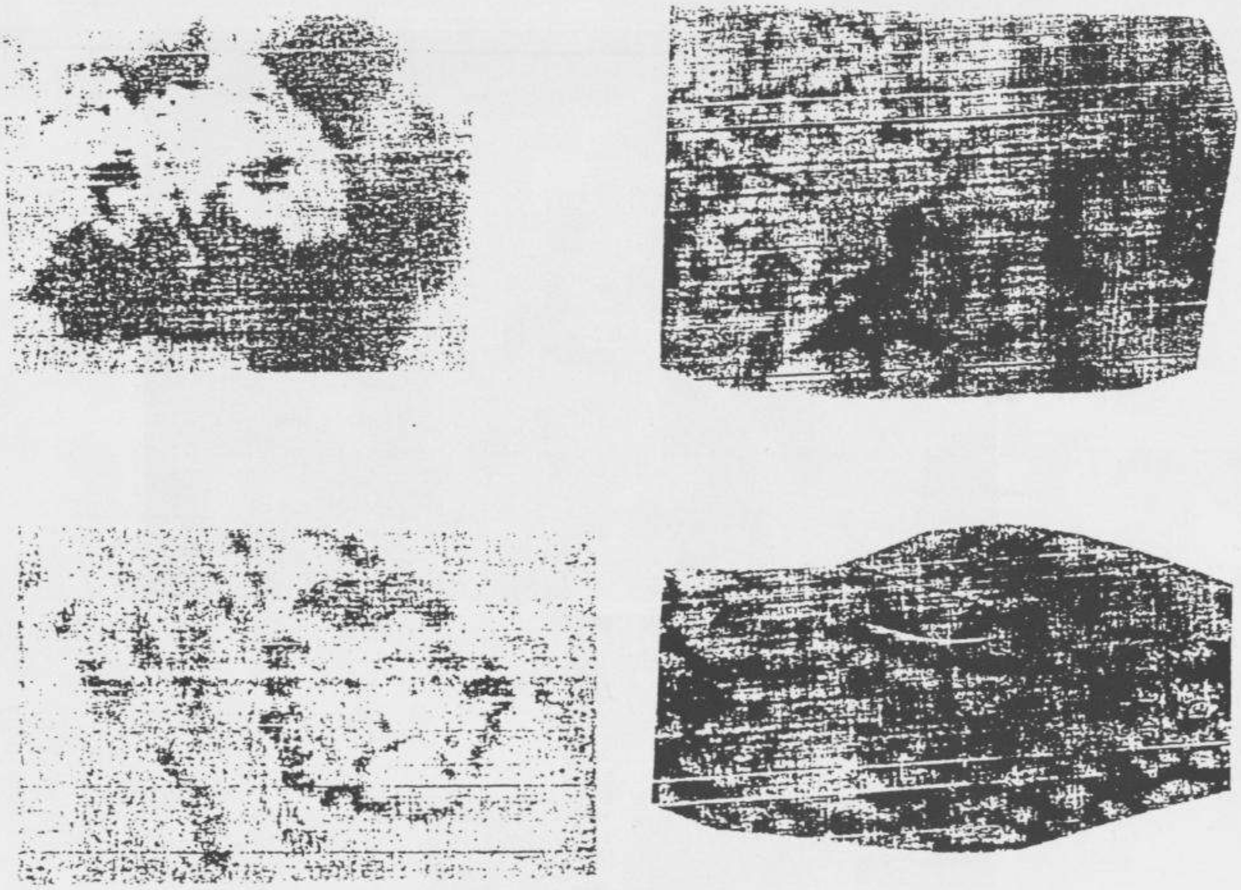

Fig. 5. Autoradiograms of plugs of halite and carnallite samples.

PETROGRAPHY OF SALTS IN COMPACTED PLUGS

Preparation of samples

Two methods were used to determine the spatial arrangement of the salts in compacted plugs of mixed salts: (a) autoradiography, and (b) staining procedures.

Autoradiography, in which radiograms are produced using the radiation from naturally occurring K^{40} has been used to show the spatial position of potassium containing salts in a mixed ore. Figure 5 shows radiograms produced from slabs of carnallite/halite mixtures made as described above, after 5 days of exposure using an intensifying screen. It can be seen that the contrast in these radiograms are not good, although it can be improved by longer exposures.

Staining procedures are based on chemical reactions which are selective for potassium or sodium ions and which produce a coloured product. It was found that the two most suitable solutions or stains for use on mixed salts of halite and carnallite or halite and sylvite were an aqueous solution of cobalt nitrite or a 1% solution of malachite in chloroform based on the method of Reid (1969). The example shown in Fig. 6 was obtained by taking a compacted

Fig. 6. Section through a plug of halite and carnallite stained with 1% malachite in chloroform (x5)

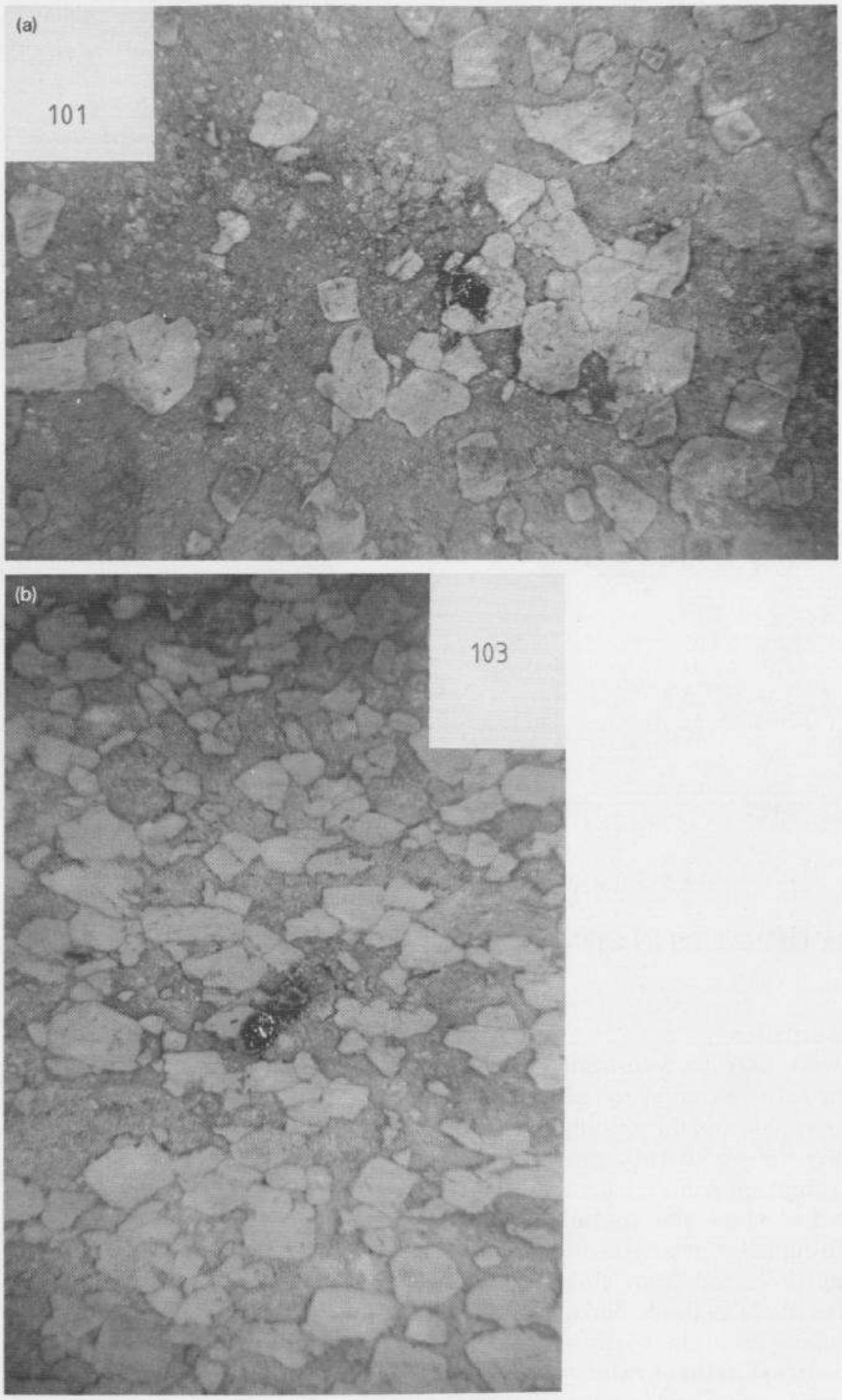

Fig. 7. Sections of a carnallite/halite plug (x5) (a) Surface of plug. (b) Section through plug from top to bottom.

mixture of carnallite and halite, polishing the area to be stained, wiping the polished surface with a tissue wetted in distilled water, adding a small amount of 1% malachite in chloroform to the surface and allowing the solvent to evaporate.

This procedure produced a green stain in the carnallite while the halite remained colourless. Also the carnallite crystals were partially dissolved, resulting in a slight relief, which allowed carnallite to be differentiated from sylvite.

As the staining reaction gives better contrast than the radiograms and because samples could be prepared much faster, this was the method chosen for preparing samples for the petrographic studies.

PETROGRAPHIC STUDIES

Plugs were prepared of 88% carnallite, of 100% halite, of 84% sylvite, and of 55% carnallite and 45% halite. These plugs were cut into sections both along the direction of application of the compacting pressure and at right angles to the pressure at several positions from the top to the bottom of the plug. The exposed faces were stained using the procedure outlined above. Two sections from a single plug are shown in Fig. 7 for a mixed carnallite/halite plug. The following effects can be distinguished:

(a) the halite crystals are partially oriented with their long axes perpendicular to the direction of applied pressure.

(b) the grain boundaries of the carnallite have been lost and the carnallite appears to have flowed into the pores between the halite crystals. In most cases the halite crystals have maintained their original shape.

(c) although the salts were well mixed prior to forming the plugs, the salts are not evenly distributed within the plugs. The halite content inside the plug is higher than on the surface of the plug.

These observations suggest that the carnallite has moved preferentially by plastic flow. The orientation of the halite crystals and their uneven distribution is likely to have an effect of the dissolution kinetics of the mixed salts and they imply that it may be difficult to prepare reproducible synthetic cores for dissolution tests.

In the compacted plugs of 88% carnallite the grain boundaries of the carnallite are still visible but the crystals have become distorted as shown in Fig. 8a. A similar distortion is seen in compacted plugs of 100% halite as shown in Fig. 8b.

DISSOLUTION STUDIES

The method of Cofman (1931) was used for the dissolution studies. Samples of synthetic ores were sealed in polyester such that only one face was exposed and, after being weighed in air, the sample under test was suspended from an automatic balance in a large volume of the dissolution brine in a thermostatic bath. The surface of the dissolution brine was covered with plastic balls to reduce heat losses.

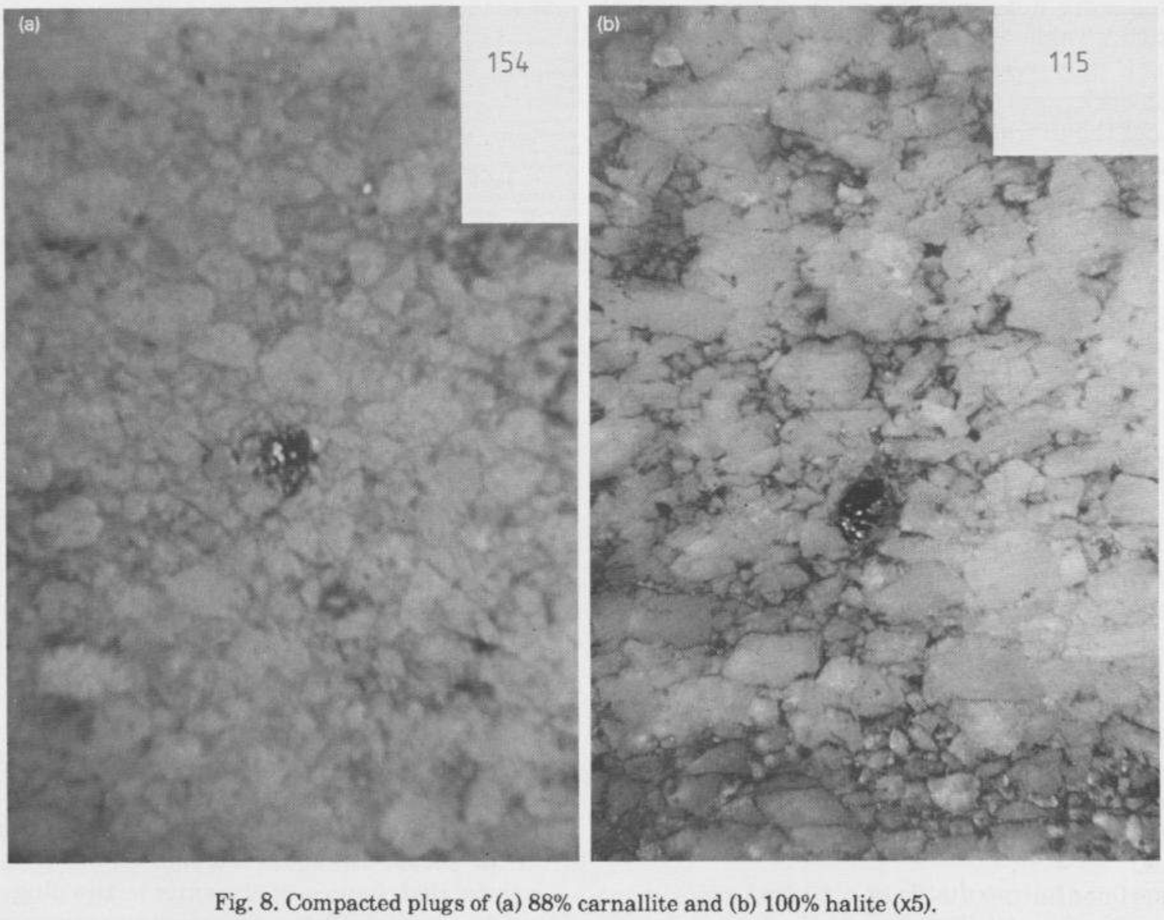

Fig. 8. Compacted plugs of (a) 88% carnallite and (b) 100% halite (x5).

The change in weight of the sample with time was recorded automatically on a personal computer. The density of the dissolution brine at the mid-height of the plug was measured at regular intervals (to allow the true weight of the sample in air to be calculated) and was found to change very little during the course of an experiment. At the end of an experiment the weight of the dried sample in air was measured.

Experiments were carried out to determine the effects of temperature, solid composition and composition of the brine on the dissolution rates. In all cases the dissolution rate was measured for the case of dissolution from a horizontal surface (dissolution brine under the dissolving face).

The results fall into three classes: those for single salt, and those for mixed salt plugs in unsaturated and saturated NaCl brines.

DISSOLUTION KINETICS FOR SINGLE SALTS IN UNSATURATED BRINES

The dissolution kinetics of halite, carnallite and sylvite were measured in tap water and brines containing 13% NaCl at 40°C and compared with values from Rohr (1980). The samples of sylvite and carnallite used were not pure as shown in the chemical analysis in Table 1; however, they appeared to behave as if they were essentially single salts. As the present work examined dissolution of horizontal surfaces and the literature values are for dissolution of vertical faces, the literature values were multiplied by 1.44 which is the ratio of the difference in rates given in Saberian (1981). The literature rates were converted from 20°C to the expected rates at 40°C using the temperature effects on the dissolution rates from Karson (1954). The temperature dependence of the rate of dissolution of carnallite was assumed to be the same as that of sylvite. The results are given in Table 2 and show a reasonable agreement with those expected from the literature, considering the approximations used. Some of the differences observed may be due to the fact that the salts used were impure or due to differences between the rates of dissolution of horizontal and vertical faces.

The results from a typical experiment are shown in Fig. 9.

Dissolution kinetics for mixed salts in undersaturated brines

The dissolution rates of mixed plugs of carnallite, sylvite and halite were measured in pure water at different temperatures and the results are given in Table 3.

Experimental results from a typical experiment are given in Fig. 10. The dissolution rate remained almost constant throughout an experiment as in the case of dissolution of a single salt. However, the dissolution of mixed salt plugs differed from that of dissolution of single salt plugs in that the dissolution rates for different plugs were not consistent with the rates expected, for example, the dissolution rates for plugs of 55% carnallite/45% halite in water did not increase with temperature as expected. This behaviour is thought to be due to differences in the petrography of the plugs, e.g. small changes in the porosity and spacial distribution of the salts in the plug. Further work to explain these differences is in progress.

TABLE 2

Dissolution rates of single salt plugs at 40°C (t/m^2/year)

Salt plug	Dissolution brine			
	Water		13% NaCl in water	
	Measured	Literature	Measured	Literature
88% Carnallite	720	640		350
83% Sylvite	340	400	300	200
100% Halite	260	410	210	160

TABLE 3

Dissolution rates of mixed salt plugs in water (t/m^2/year)

Salt plug	Temperature		
	25°C	40°C	60°C
55% Carnallite/45% halite	710	1100	740
35% Carnallite/65% halite	600	900	1100
45% Carnallite/10% sylvite/45% halite	410	410	500

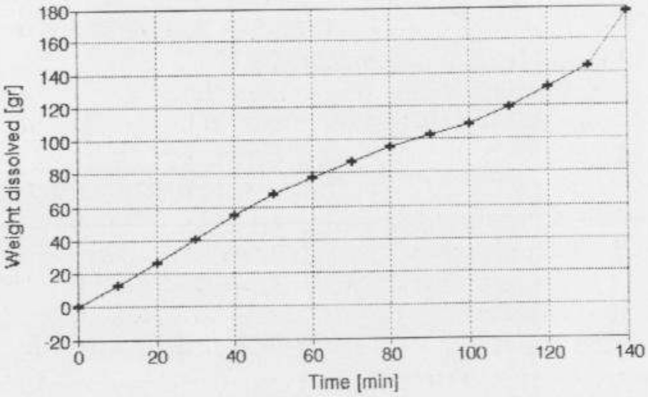

Fig. 9. Test 36: 100% halite in water at 40°C.

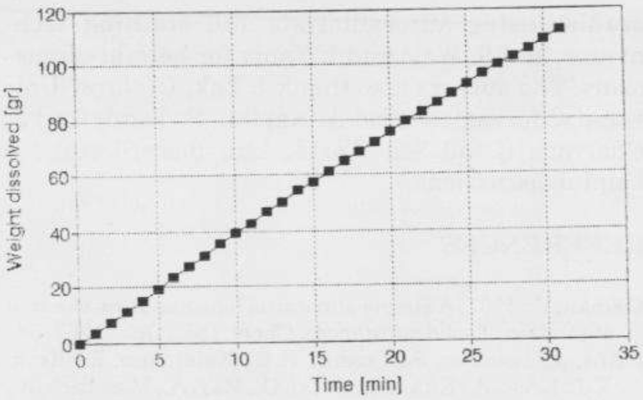

Fig. 10. 45% Carnallite, 45% NaCl, 10% KCl in water at 25°C.

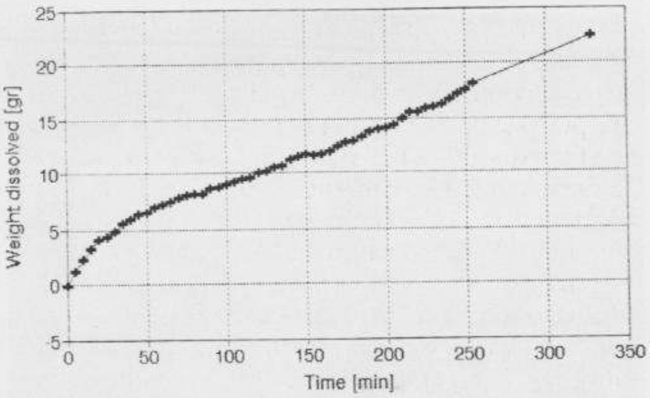

Fig. 11. Test 24: 53% carnallite and 47% halite in saturated NaCl at 60°C.

The dissolution rates appear to be almost as rapid as the dissolution rate for the salt which dissolves fastest.

Dissolution rates in saturated brines

The dissolution experiments were carried out in water saturated in NaCl. The graphs of weight change against time show two types of behaviour:

(a) Those where the weight changes in an approximately linear fashion with time. This type of behaviour was only observed for plugs with a high percentage of carnallite at high temperatures. An example is shown in Fig. 11. Very little deposition of halite was seen on the plugs.

(b) Those where the weight changes in a non-linear fashion with time, as shown in Fig. 12. These experiments were often accompanied by the presence of salt stalactites growing from the dissolving face of the salt plug as shown in Fig. 13. Analysis of these stalactites showed that they consisted mainly of halite with less than 2% $MgCl_2$ and KCl. Crystallization of halite from NaCl saturated solution is expected when $MgCl_2$ and KCl dissolve since they reduce the solubility of halite (D'Ans et al., 1962). The results of the experiments where the weight varied linearly with time are given in Table 4.

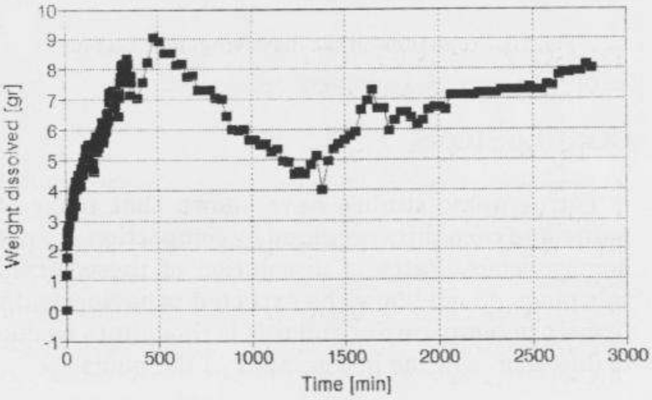

Fig. 12. Test 22: 35% carnallite and 65% halite in saturated NaCl at 40°C.

TABLE 4

Dissolution rates in saturated NaCl brines where the weight changed linearly with time

Plug composition	Temp. (°C)	Dissolution rate (t/m^2 year)
88% Carnallite	60	110
55% Carnallite/45% halite	60	12

More detailed examination of the dissolution plot in Fig. 11 shows that it consists of micro-steps where at times the dissolution almost stops and at others it proceeds at a faster than average rate. This stepwise progress appears to be caused by changes in the face presented to the dissolution brine as the salt crystals fall from the face and expose new areas of carnallite to dissolution.

The initial rate of dissolution is higher than the average rate and this may be caused by an uneven distribution of carnallite throughout the plugs as seen in Fig. 7.

The results from the experiments where the weight changed in a non-linear fashion with time cannot be used to derive dissolution rates as the weight change is the difference between the weight of the salt dissolved and the salt deposited. Future experiments will determine the dissolution rate for these cases by chemical analysis of the dissolution brine.

One effect that was observed with experiments where salt stalactites were formed was that there were occasional, rapid changes in weight. This seemed to be associated with stalactites falling from the plugs.

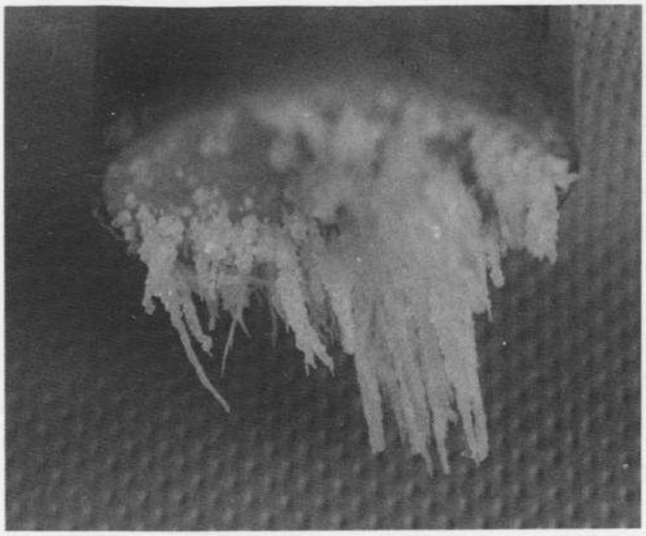

Fig. 13. Stalactites on the dissolving face of a plug.

CONCLUSIONS

Petrographic studies have shown that plugs of halite and carnallite prepared by compaction are not homogeneous. Rates of dissolution of these mixed salt plugs do not show the expected behaviour with respect to temperature and this is thought to be due to differences in the petrography of the plugs.

ACKNOWLEDGMENTS

The authors wish to thank the following IMI staff: R. Cytermann and A. Cremer for measuring the mechanical properties of the salts, R. Almog, S. Plotnityzki, M. Abramovich and C. Zeleznik for assistance in measuring dissolution rates, G. Lieber and T. Wiegner for assistance with the petrographic studies using autoradiolysis and staining techniques, and S. Wajc and I. Yaniv for helpful discussions. The authors also thank I. Zak, (Hebrew University, Jerusalem) and A. Kaplan, S. Tandy and J. Charrach (Dead Sea Works, Ltd. Beer-Sheva) for helpful discussions.

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