

Methodical Investigations on the Origin of Brines in Salt and Potash Mines

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ABSTRACT

All investigations on solution influx in salt and potash mines are based on two main questions: 1) Which genetic processes formed the brines, and 2) where are the reservoirs from which the brines penetrate the evaporites. A scheme describes all the major information which is necessary for final results on the origin of brines in salt and potash deposits. The technique for sampling brines in salt mines is explained. Three computer programs are outlined for investigations on the occurrence and the origin of brines in potash and salt mines: The program SALZLOESUNG (salt solution) for calculation all the analytical and physio-chemical data which are necessary for genetic interpretations; program SALZBANK (salt bank) for storing and recalling the data which are calculated by the program SALZLOESUNG; program LOESUNGSMET (solution metamorphism) for calculating the alteration and mass balance of major and minor components distributed in brines and the evaporites.

INTRODUCTION

One of the major problems in underground mining is the possibility of water or solution influx in salt and potash mines (e.g. Baumert, 1928). Economic important minerals like halite, sylvite, carnallite, and kainite belong to the most water soluble compounds of the upper earth's crust. Therefore all evaporites with associations of the mentioned minerals are very sensitive to reactions with unsaturated solutions infiltrating salt deposits. Since the beginning of underground potash mining about 120 years ago, solution influx into the mine openings were the reason for limiting the resources of salt deposits, either because of need for special safety salt rock pillars or by stopping all mining operations in the case of flooding the mine. Baumert (1952) estimated a loss of resources in Germany due to salt mines flooding during a mining period of 90 years to be 100 million tons of K_2O . This value corresponds to 20 times the annual K_2O production in both the Federal Republic of Germany and the GDR. Both numbers give an idea of the importance of all the problems in connection with the origin and the influx of brines in salt and potash mines.

BRINE CLASSIFICATION

All investigations on solution infiltrations in salt deposits are based on two main questions: 1) Which genetic processes formed the salt solutions, and 2) where are the reservoirs from which the solutions penetrate the evaporites. The present paper is restricted to some methodical aspects and a special scheme of investigation for determining the origin of brines in salt and potash mines.

First of all one must know which groups of brines participate as solution influxes in salt deposits (e.g. Herrmann, 1961; Kockert, 1968). It seems suitable to distinguish between 3 groups of salt solutions with respect to practical aspects at which mixed solutions between and within the different groups are possible (Table 1). All the solutions which are dangerous for underground mining operations belong to group 1. In contrast the solutions of groups 2 and 3 are less or not dangerous for underground mining in salt deposits.

The localities for the different groups of salt solutions are drawn schematically in Figure 1. For example surface water and ground water are located near the earth's surface.

TABLE 1
Salt Solutions in Salt and Potash Mines. Possibilities of Their Occurrence and Origin

Group 1 Geology, Deposition	Group 2 Mining	Group 3 Salt Production
1.1 Surface water and ground water	2.1 Shaft brines	3.1 Brines from backfill materials
1.2 Formation water	2.2 Condensate of the ventilation air	3.2 Solutions from the salt production
1.3 Metamorphic solutions	2.3 Drilling fluid	
1.4 Hypothetical residual solutions from the evaporation of sea water (so-called 'Urlaugen')	2.4 Residual brines from the bottom of the shaft	

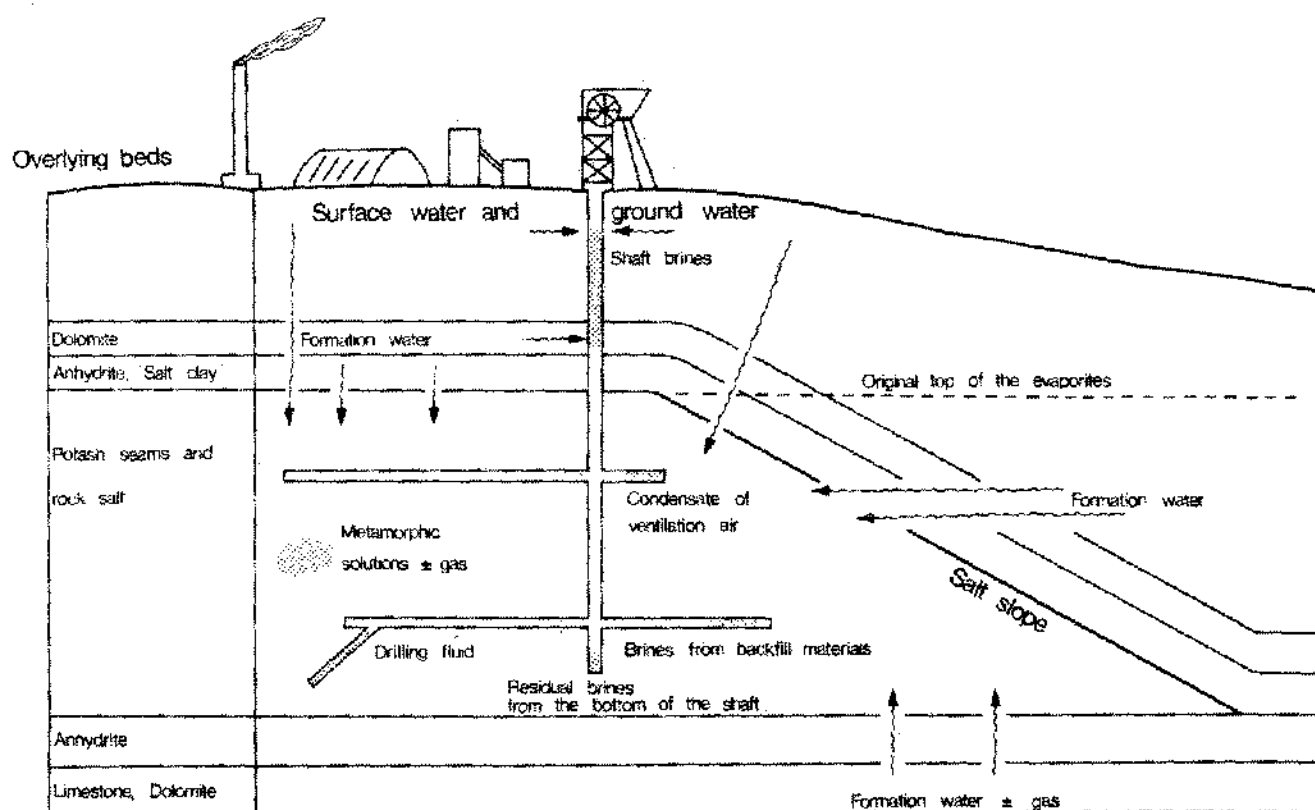


Figure 1. Localities for the different groups of salt solutions (Herrmann et al., 1978).

Formation water and gases are present in the rocks surrounding the salt deposit, drilling fluids occur in the mine openings, and shaft brines at the bottom of the shaft.

All the major information which is necessary for final results on the origin of brines in salt and potash deposits are summarized in Figure 2. At the top of all information, the sampling of salt solutions and gases must be mentioned. It is important to note that the chemical composition and the concentration of the solutions are identical with the brine which actually penetrates the evaporites. Solutions which are not representative of the brine influx found at mine

openings are the reason for wrong conclusions, this is especially true for the points at the left hand side of Figure 2. The chemical analysis of the solutions with data about the major components and trace elements. Analysis of gases are necessary in the case of gas migration together with solution influx. 2) The calculation of special data (e.g. mol compounds/1,000 mol H_2O and others) and the classification of the solutions will be also influenced by solutions which are not representative of the real brine compositions occurring in the salt deposit.

In contrast, the following information is independent

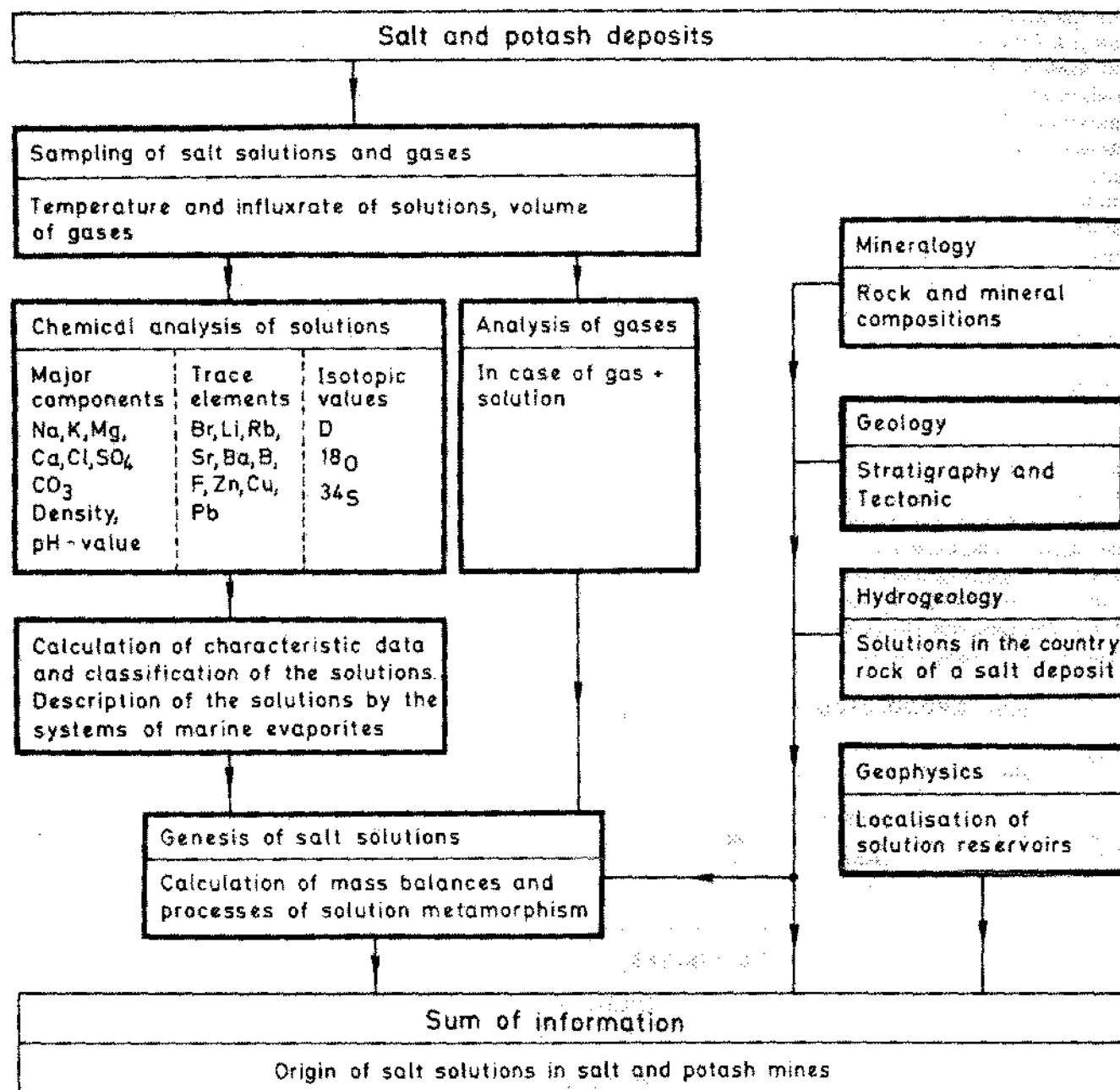


Figure 2. Information necessary for results on the origin of brines in salt and potash deposits.

from the sampling technique of solutions and gases: The mineralogy with data about the rock composition and mineral associations distributed in the salt deposit; the geology with information about the stratigraphy and tectonic situation of the salt deposit and the surrounding country rock; the hydrogeology with data about the occurrence and composition of solutions in the country rock around the salt deposit; the geophysics with methods for localization the solution reservoirs.

The following discussion is limited to the information written at the left hand side of Figure 2. Because all infor-

mation and conclusions about the origin on salt solutions are dependent on the accuracy of the solution sampling technique it seems necessary to discuss this problem first.

SOLUTION SAMPLING TECHNIQUE

The solution influx in salt mines is limited either to small localities or areas where brines are infiltrating and penetrating larger parts of the salt deposit. In both cases water begins to evaporate at the moment of contact between solution and air ventilation in the mine at which the concentra-

tion and the chemical composition of the solution can be changed. Experimental results of water evaporation by solution sampling in salt mines are given in Figure 3. Three kinds of open plastic vessels with different surface diameters were used for the experiment: Dishes with a surface of 346 cm² (diameter 21 cm), beaker with a surface of 87 cm² (diameter 10.5 cm), and bottles with a surface of 3 cm² (diameter 2 cm). Each vessel was filled with 1,000 g of a carnallite saturated solution from the fabrication of potash salts in Salzdetfurth. The experiment was carried out at the 1,190 m level of the salt mine Niedersachsen-Riedel at an average air temperature of 30°C. The experiment was finished after 16 days. Samples for the chemical analysis were taken after 1, 2, 3, 8, 13, and 16 days. The upper part of Figure 3 demonstrates the amount of water evaporation depending on the surface of the sampling vessels. From 1,000 g solution in the dish at the beginning of the experiment 127 g or 13 wt.-% H₂O are evaporated 24 hours later. Only 42 g or 4 wt.-% H₂O are evaporated in the same time from the beaker and no change in the brine concentration and chemical composition was obtained in the bottle. The same results are demonstrated by the solid phases crystallized from the brines during water evaporation (middle part of Fig. 3). The solid phases are calculated as carnallite,

kieserite, and halite. Concentration and chemical composition of the solutions in the dish and the beaker are changed drastically during the first 3 days. In contrast no variation of the solution composition in the bottle was measured during the whole 16 days of the experiment. In the lower part of Figure 3 information is given about the amount of remaining solution after water evaporation and crystallized solid phases. For example the remainder of a 7,000 g solution as starting weight in the dish was determined 3 days later to be 678 g brine. These data demonstrate the importance of the sampling technique in deriving conclusions about the origin of salt solutions especially if the influx rate is very low (few milliliters or drops per minute, long sampling time) and sampling vessels with large surfaces are used. Therefore uniform instructions are given from the Kali und Salz AG in Germany for sampling brines and measurements of temperature, air ventilation etc. at the locality of brine influx in mine openings.

COMPUTER PROGRAMS

After brine sampling, the solutions and gases are analyzed for major components and specific trace elements. For investigations on the occurrence and origin of brines in

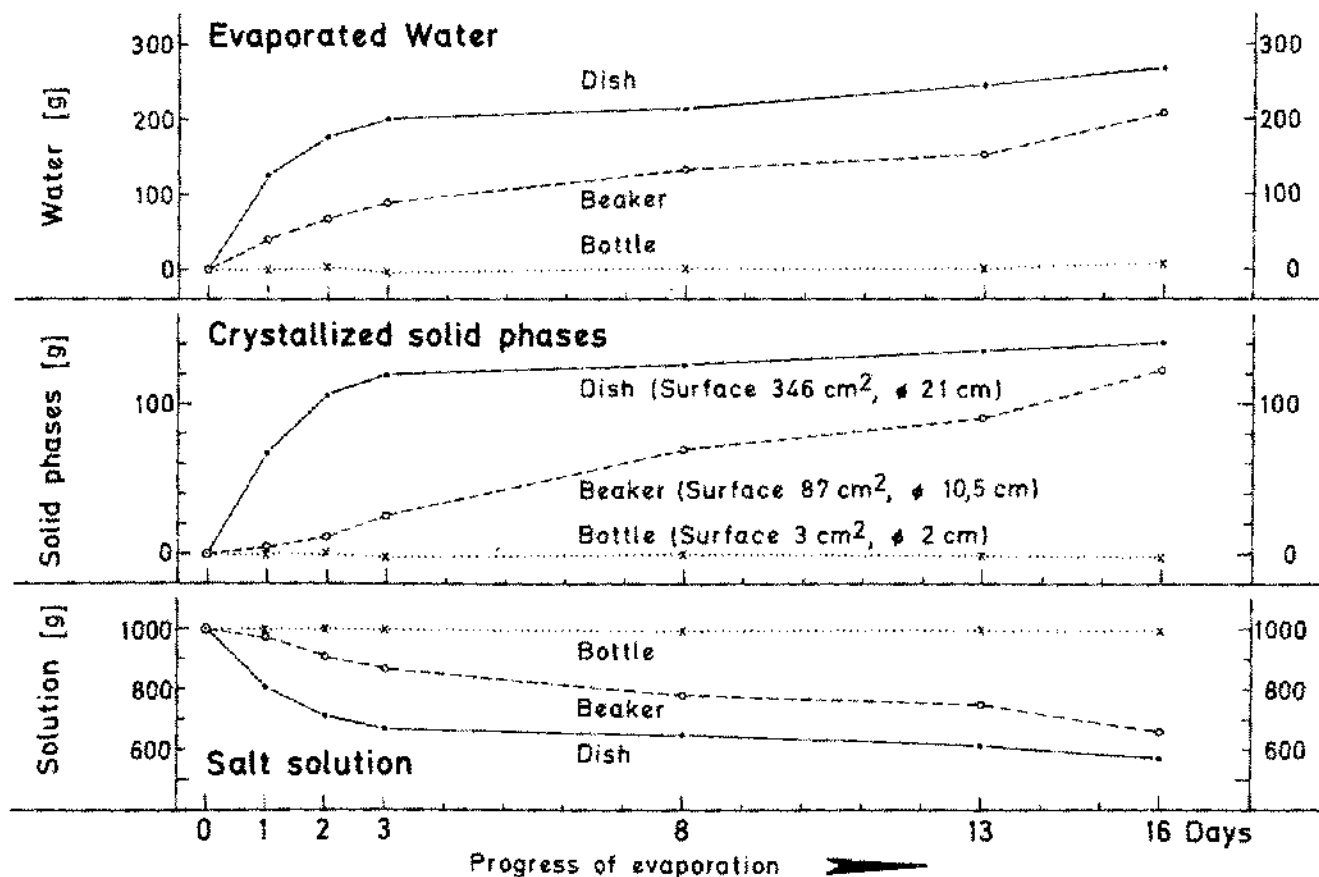


Figure 3. Experimental results of water evaporation by solution sampling in salt mines.

potash and salt mines the following data must be calculated: mol cations, anions, and compounds/1,000 mol H_2O , mol percent and equivalent percent cations and anions, mol-equivalent cations and anions, and Jänecke mol percent values for equilibrium solutions of the marine five-component system at NaCl saturation. A computer program SALZLOESUNG (salt solution) was developed for calculating all these data using the chemical analysis of brines (Herrmann et al., 1978).

The concentration and the chemical composition of brines are also classified by the program SALZLOESUNG (Table 2). The classification scheme informs one about the possibility and probability of solutions that dissolve and react with evaporites. Such information is important in salt mining. The concentration of the brines is characterized by classifying the data as g salt/100 g solution (wt.-%) in five major groups: 1) up to 0.1%; 2) > 0.1–3.5%; 3) >3.5–14%; 4) >14–27%; 5) >27%. The chemical composition of a brine can be symbolized by one of the four subgroups A, B, C, and D. The subdivisions point out whether in a specific major group NaCl, KCl, or $MgCl_2$ dominates or whether a $CaCl_2$ content is calculated for the brine (Table 2). The advantage of the scheme of Table 2 depends on a classification principle which is especially developed and useful for all questions about the possibility of dissolu-

tion and solution metamorphism processes in salt and potash deposits.

Analytical data for brines which are collected over many years must be available each time for new use. A program named SALZBANK (salt bank) was developed for storing all the data which are calculated by the program SALZLOESUNG (Herrmann et al., 1978). Recall of the stored data is possible after different points of view: time periods, salt deposit districts, mines, and geochemical aspects are known. In the same manner the equivalent percent of cations for a brine can be plotted with a subprogram in triangle graphics at which the concentration and the chemical composition of the solution are marked out by different symbols (Fig. 4).

Solution values for 190 points determined during a period of 60 years and from 6 deposit districts of the German Zechstein are plotted in Figure 4. The projection points represent equivalent percent cations and the different symbols refer to wt.-% of dissolved salt in solution. The majority of the points (circles and dots) are brines with a preponderant content of NaCl or $MgCl_2$. In contrast, only few values with symbols for salt concentrations of <14 wt.-% are plotted in Figure 4. But all the saturated brines are not in each case less dangerous than unsaturated solutions. The experience of over 100 years in underground

TABLE 2
Salt Solutions from Salt and Potash Mines. Scheme of Classification (Herrmann et al., 1978)

Classification Code	Groups of Salt Solutions	mol/1,000 mol H_2O	Total salt content		Density (20°C)
			g/100 g solution (wt.-%)	g/1,000 ml solution	
I	Fresh water	—	up to 0.1	up to 1	up to 1.001 ± 0.0005
2A	Salt water	NaCl solution	NaCl > KCl and > $MgCl_2$	>0.1 – 3.5	>1 – 35
2B		KCl solution	KCl > NaCl and > $MgCl_2$		1.03 ± 0.01
2C		$MgCl_2$ solution	$MgCl_2$ > NaCl and > KCl		
2D		$CaCl_2$ solution	$CaCl_2$ > 0		
3A	Low concentrated solutions	NaCl solution	NaCl > KCl and > $MgCl_2$	>3.5 – 14	>35 – 150
3B		KCl solution	KCl > NaCl and > $MgCl_2$		>1.02 – 1.11 ± 0.01
3C		$MgCl_2$ solution	$MgCl_2$ > NaCl and > KCl		
3D		$CaCl_2$ solution	$CaCl_2$ > 0		
4A	Concentrated solutions	NaCl solution	NaCl > KCl and > $MgCl_2$	>14 – 27	>150 – 350
4B		KCl solution	KCl > NaCl and > $MgCl_2$		>1.10 – 1.24 ± 0.02
4C		$MgCl_2$ solution	$MgCl_2$ > NaCl and > KCl		
4D		$CaCl_2$ solution	$CaCl_2$ > 0		
5A	Highly concentrated solutions	NaCl solution	NaCl > KCl and > $MgCl_2$	>27	>350
5B		KCl solution	KCl > NaCl and > $MgCl_2$		>1.22
5C		$MgCl_2$ solution	$MgCl_2$ > NaCl and > KCl		
5D		$CaCl_2$ solution	$CaCl_2$ > 0		

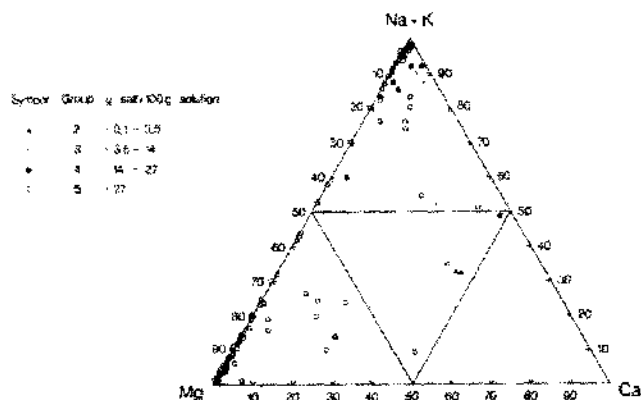


Figure 4. 190 brines analyzed during a period of 60 years and from 6 deposit districts of the German Zechstein.

potash mining has shown that saturated brines can change the salt concentration and the chemical composition by becoming unsaturated solutions. In the case of solution influx in mine openings it is very important to notice such a situation ahead of time.

The major components of salt solutions can be characterized in the following manner: Rock salt deposits by the system $\text{NaCl-H}_2\text{O}$; potash deposits of the sulfate type by the five-component system $\text{NaCl-KCl-MgCl}_2\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ at NaCl saturation; potash deposits of the chloride type, subtype sylvite + carnallite (Herrmann, 1977), by the four-component system $\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$ at NaCl saturation. Besides the major components, values for the following trace elements are necessary for investigations on the origin of salt solutions: Br, Li, Rb, in special cases B, J, Pb, Cu, Zn, and others and the isotopic values ^{18}O , D, ^{34}S . The methods and possibilities using major and minor components for a geochemical judgment of brines from salt and potash deposits are known (e.g. Herrmann, 1961; Koch et al., 1968; Müller and Papendieck, 1975). A computer program allows the calculation of all theoretical possibilities for solution metamorphism processes and mass balances of major components and the distribution of Br in minerals and brines for the case of reactions between unsaturated solutions and evaporites in salt deposits and potash deposits of the sulfate and chloride type. Another function of the program allows a comparison between the calculated and the real rock composition of the salt deposit. The program is named LOESUNGSMET (solution metamorphism) and described by Herrmann et al. (1978). Using the program only a short time is necessary to calculate data for all theoretical thinkable connections between brine influxes in the mine openings, and the existence of fossil or recent formation waters, ground waters, and others. The different functions of the three mentioned computer programs (SALZLOESUNG, SALZBANK, LOESUNGSMET) are a logical unit for all physico-chemical and geochemical calculations and investigations on the origin of brines in salt and potash deposits.

CONCLUSIONS

It stands to reason that computer programs at the present time cannot replace the critical examinations of all calculated brine informations by geoscientists. The present advantage of the programs is the possibility of calculating reactions and processes using the extensive and each time available archive of chemical brine analysis. In future more chemical work must be done for a better classification of the different groups of salt solutions using special trace elements and isotopic values. After that it seems possible to develop a computer program which calculates and prints out the complete result on the origin and occurrence of a brine influx in salt mines. Such an idea sounds like science fiction in the present time. But maybe the first step in this direction has already been accomplished with the described computer programs. We will also continue further work on this problem.

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