ENVIRONMENTAL AND ARTIFICIAL TRACERS FOR INVESTIGATING LEAKAGES INTO SALT MINES

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Abstract

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The paper presents the results of five years of experience in investigating the origin of waters in the Wapno mine, where salt is exploited in a Zechstein dome, in northwestern Poland. Tritium and ^{14}C measurements showed young infiltration waters in leakages at the third level of the mine. Stable isotope determinations showed a considerable shift of values from the precipitation line, both on activity and on concentration scales. Despite this shift, it was possible to distinguish infiltration waters from connate ones appearing at deeper mine levels. In 1976 and 1977 leakage flow-rates increased and the mineralization decreased. Tritium and ^{14}C contents did not then change, showing that, at the initial stages of flooding, the origin of water in the leakages was not changed. The first results of isotope investigations in the Kłodawa mine, situated in another Zechstein salt dome in central Poland, showed connate waters. Observations performed in the Wieliczka salt mine, situated in Miocene formations in southern Poland, showed old waters originating from the surrounding formations. Their stable isotope composition shows that recharge took place in a cooler climate. The ^{14}C content of these waters is 1 to 2% of recent carbon. The experimental procedure used to determine the isotopic composition of highly mineralized brines is also described.

INTRODUCTION

The origin of waters occurring in mines is of interest for geochemistry and of importance to mining hydrology, particularly for its safety aspects. The main aim of this work was to determine the hydraulic connections and the origin of brines in the Wapno salt mine. The investigations were performed with the aid

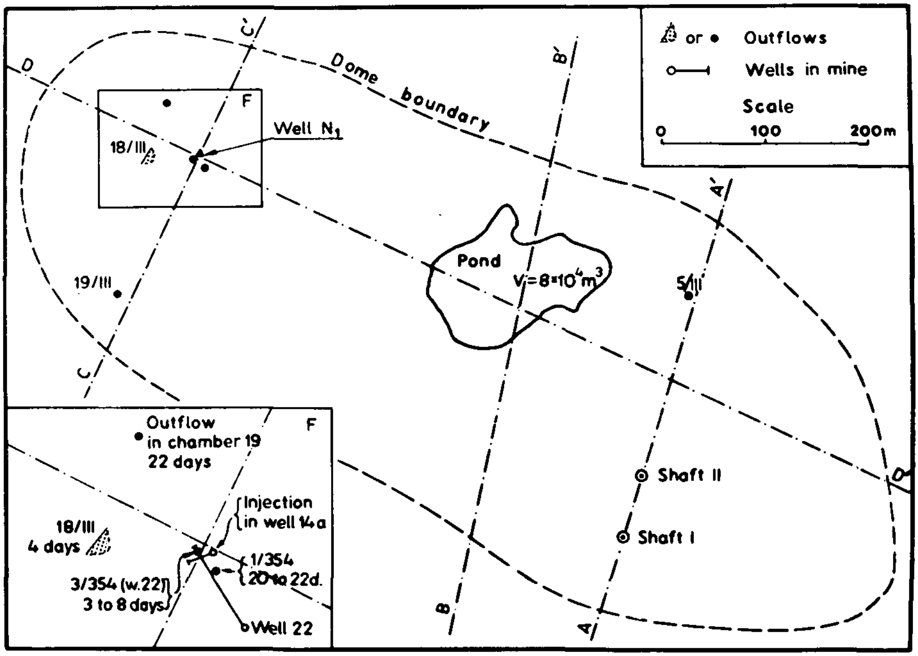

FIG.1. Wapno dome: the main sampling points.

of environmental isotopes and artificial tracers. Preliminary results obtained in the Kłodawa salt mine are also given. These investigations were to determine if any leakages originate from the surrounding formations.

In the Wieliczka mine, the third investigated salt mine, the investigation was aimed at determining if the leakages come only from the surrounding formations, or if some are of infiltration origin.

Measurements of the isotopic composition of highly mineralized brines have seemed troublesome. With oxygen the isotopic composition was measured in terms of activity, and the concentration was calculated. On the other hand, the deuterium content was measured in terms of concentration, and the activity was calculated.

1. THE WAPNO SALT MINE

1.1. Geology and history of the mine

The Wapno mine is situated in the smallest salt dome in Poland, in the north central part of the country. Figures 1, 2 and 3 show a simplified geological

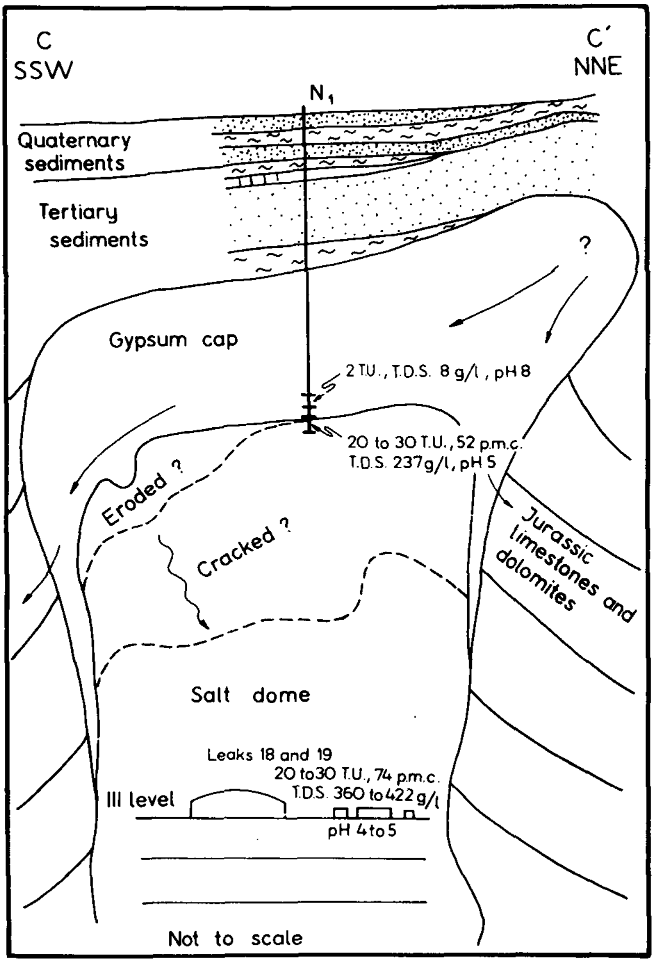

FIG. 2. Cross-section C-C' of the Wapno dome.

situation. The central part of the gypsum cap reaches the ground surface where there was an old gypsum mine (levels I and II).

The dome is surrounded by Jurassic limestones and dolomites, which are probably permeable, especially at fault zones. Above the Jurassic formations are Cretaceous sands, margles and limestones. Around, and above the upper part of the gypsum cap are Tertiary sands, clays and brown coal, and Quaternary sediments. Generally, one water level was observed above the salt deposit, though undoubtedly there existed zones of separated stagnant water. The total amount of water present above the deposit was estimated at $2.5 \times 10^6 m^3$;

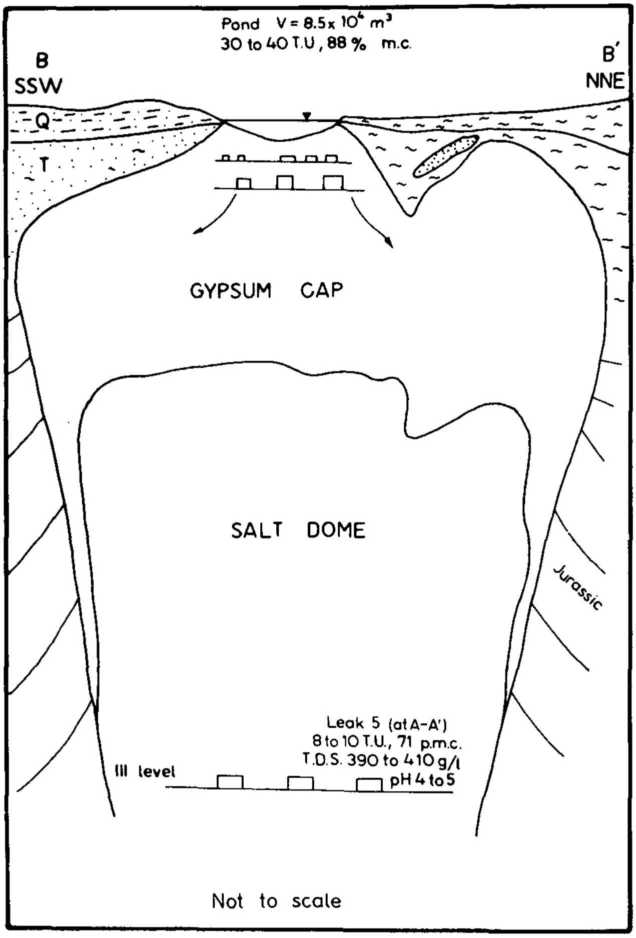

FIG. 3. Cross-section B-B' of the Wapno dome. (m.c. = modern carbon).

however, during the flooding this amount was found to be about 1.5 X 10^6 m^3. The area above the dome was recharged by precipitation and several ponds into which water from the staff washing rooms was discharged. The amount of the discharged tap water was about 2 X 10^5 m^3/a or more. Pond water was carried off by several ditches to the Czeszewo lake a few kilometres away. However, it is quite probable that a fraction of this water could contribute to the infiltration. The volume of the largest pond is 8.5 X 10^4 m^3.

The Quaternary aquifer is tapped a few kilometres away from the dome, at a depth of 21 to 31 m. This water was sampled twice – in May 1975 it

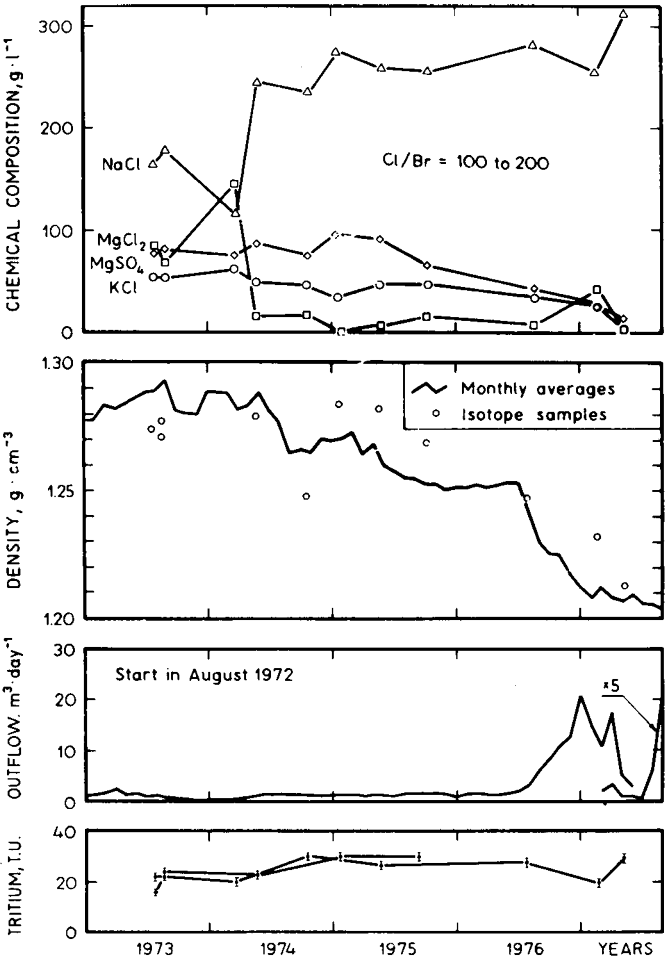

FIG. 4. Data of 18/III leakage.

showed 10 ± 1 TU, 61.7 ± 1.0 pmc ($\delta^{13}C = -11.4‰$), and $\delta^{18}O = -8.1‰$ (no δD determination), whereas in March 1978 it was 13 ± 1 TU (no ^{14}C measurement), $^{18}O = -8.2‰$, and $\delta D = -62‰$. Tertiary and deeper waters in the vicinity of the dome were not sampled.

Salt exploitation commenced in the mid-1920s at level IV (ca 400 m) and continued down to level XII (780 m). The exploitation at level III commenced in 1950. At this level there were several leakages with flow-rates less than 0.5 ml/min. The first large leakage appeared in the early 'sixties, while in the early 'seventies, the next two leakages appeared at that level in the areas where

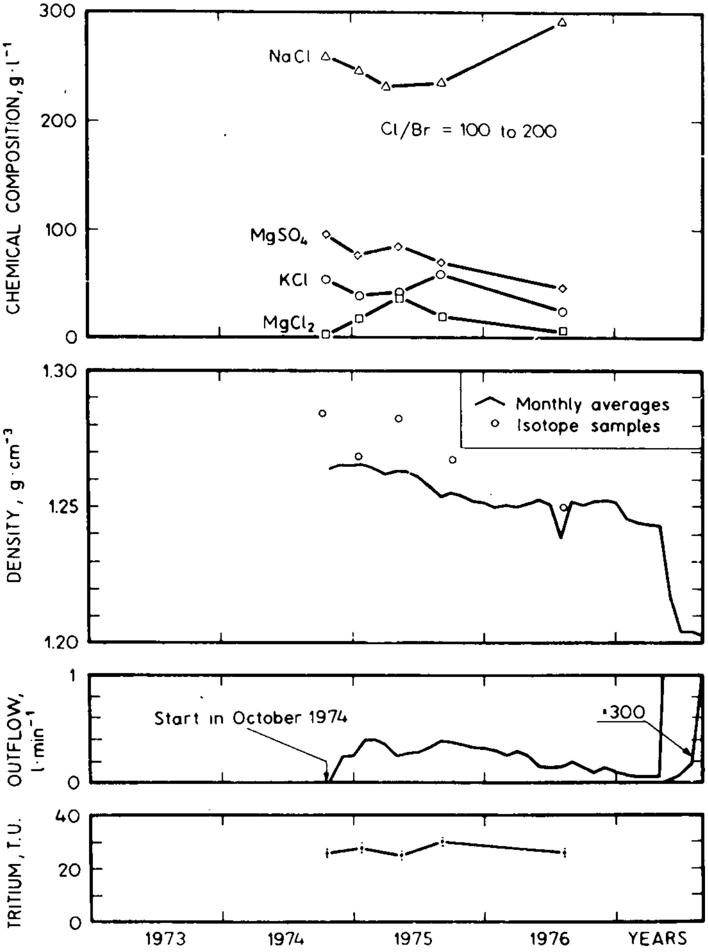

FIG.5. Data of 19/III leakage.

cavernous salts occurred. The flow-rates of the main leakages were more or less constant until 1976. In 1977 flooding became unavoidable (see Figs 4–6) and the mine ceased to exist.

1.2. Flow-rates, chemical composition and densities of brine outflows

Figures 4–6 show the mean monthly values of flow-rates of the main brine outflows at level III. The chemical composition and densities of samples taken for isotope determinations are also given. In some cases they differ considerably from the average monthly values, which were calculated from samples taken every two or three days.

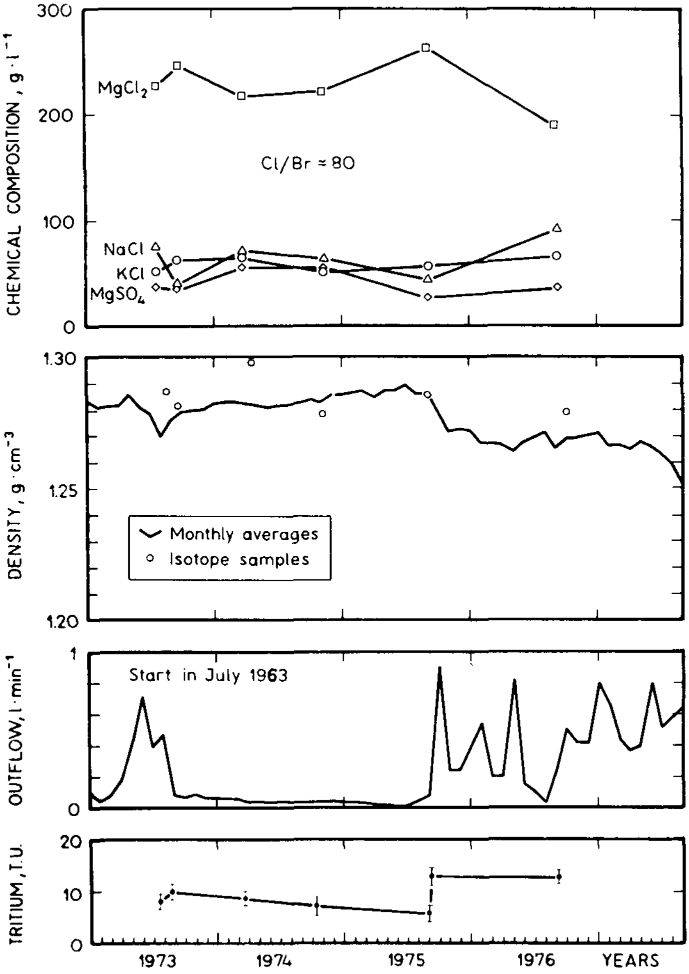

FIG. 6. Data of 5/III leakage.

1.3. Tritium and ^{14}C concentrations and their interpretation

Tritium results are shown in Figs 4–6 and repeated in Fig. 7, together with the ^{14}C results. Figure 7 also shows the results of samples from well N_1 and the largest pond. In a simplified form, without the time dependence, the same results are shown in Figs 2 and 3. From all these data it is clear that the leakages at level III were of infiltration origin.

Well N_1 was old, redrilled in 1975 because some mining engineers suspected that it had been wrongly sealed and led water to the salt deposit. During redrilling two water-bearing zones were struck. The upper zone showed low

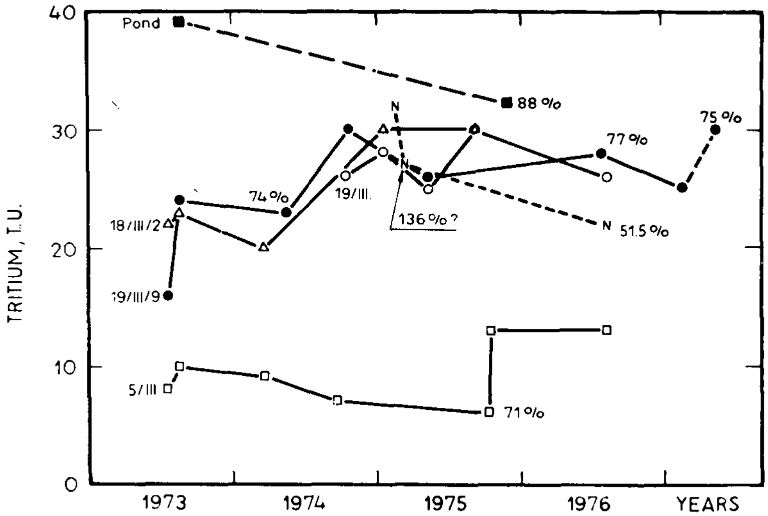

FIG. 7. Tritium and ^{14}C in the main sampling points of Wapno.

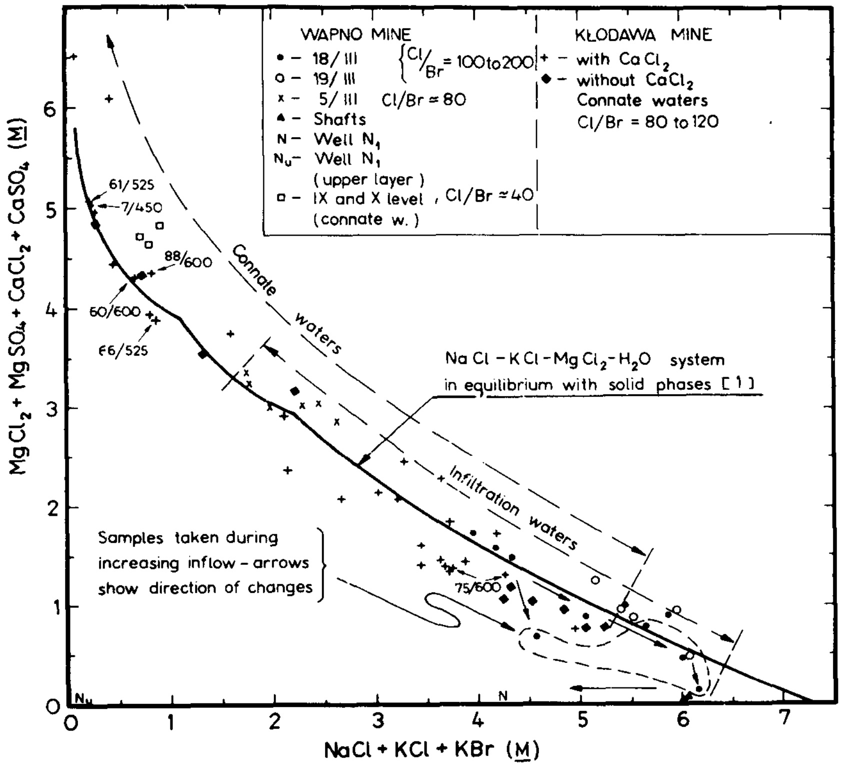

FIG. 8. Chemical relations of Wapno and Kłodawa brines.

mineralization and low tritium content (see Figs 2 and 8), while the lower one showed a high NaCl content (Figs 2 and 8). Its tritium and ^{14}C concentrations were very near the values observed in 18/III and 19/III. In other words, well N_1 showed that, at the interface of the cap with the deposit, there were waters of the same age as those in leakages 18/III and 19/III, but the well did not lead water to the dome. Undoubtedly all these waters were infiltrating directly to the gypsum cap, or through Quaternary formations. Probably there was no mixing with Tertiary waters. Water in the 5/III leakage was undoubtedly also from the Quaternary formation (high ^{14}C content) though its entrance point could not be identified.

It is difficult to calculate the mean residence time from the data of Fig. 7 since the input function cannot be well defined because the relevant parameters of the components (see Section 1.1) of the infiltrating water were not known. However, it may be assumed that the mean residence time, T, is approximately 20 years. Then, the downward flow-rate of water through the cap should be

$$Q = \frac{V}{T} = \frac{1.5 \times 10^6 \text{ m}^3}{20\text{a}} = 7.5 \times 10^4 \text{ m}^3/\text{a}$$

which is a hundred times more than the total annual inflow to the mine from 1973 to 1976 (about 600 m^3/a). A similar order of magnitude can be estimated from the known average values of the precipitation and evaporation for this part of the country, viz.

$$Q = (\text{precip.} - \text{evap.}) \times \text{area} = (0.5 - 0.4)4 \times 10^5 = 4 \times 10^4 \text{ m}^3/\text{a}$$

plus unknown amount from ponds.

It becomes clear that high tritium concentrations found in the mine and at the salt interface cannot be explained by the observed values of the leakage flow-rates. The infiltration water probably becomes mineralized in the gypsum cap and because of density effects there is a constant downward movement around the dome to the deep surrounding formations. Only a very small fraction of this water entered the salt deposit through cracks and porous salts. At the final stages, when the cracks increased, some parts of the salt dome collapsed and Tertiary waters flooded the mine. This caused a serious land subsidence above the dome, but not in the central part, where the stiff gypsum cap was not influenced. At this stage the water in the gypsum cap and in the Quaternary formations above the dome disappeared. Quaternary waters around the dome were not influenced, which confirms the assumptions concerning the infiltration through the formations above the dome. The separation of the Quaternary waters around the dome results from the elevation of the Tertiary and Quaternary formations, caused by the upward movement of the dome (e.g. see Fig. 2).

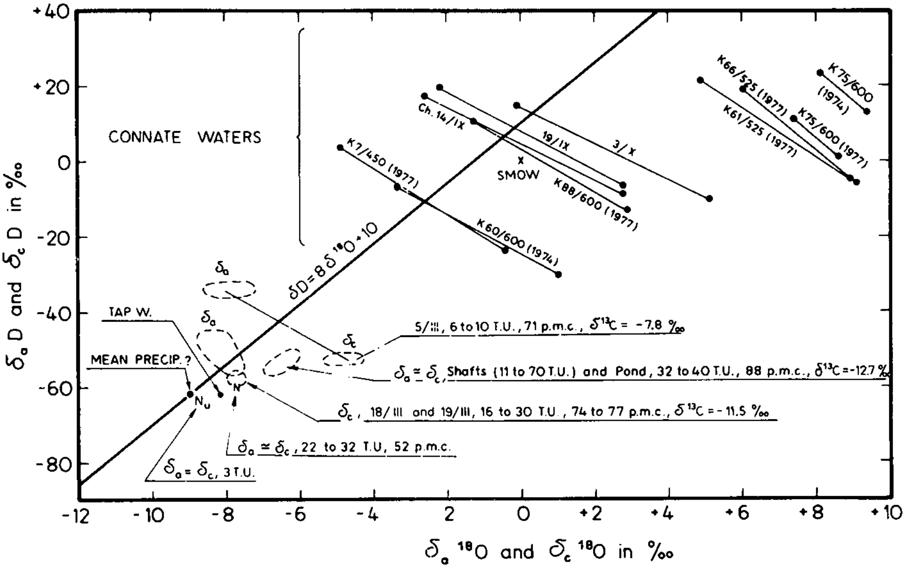

FIG. 9. Isotope activities (δ_a) and concentrations (δ_c) of Wapno and Kłodawa (K) brines.

1.4. Isotope composition

The experimental procedure used to determine the isotope composition of brines is described in Appendix 1. Figure 9 shows results of the determinations expressed in terms of both activity and concentration. Results of the 18/III, 19/III and 5/III leakages are based on numerous samples. Shafts and pond results are not certain since, in both cases, they are based on double samples only. Sample N (well N_1) is an average of three samples with a very low scatter, whereas all the other results are based on single samples. The isotopic composition of the precipitation was not measured. The precipitation point in Fig. 9 shows the expected value for the area. Tap was measured twice, as described in Section 1.

It is difficult to explain the large shift of δ_c values of the main leakages from the precipitation line. In this case it can be due to any of five reasons: (1) dissolution of hydrated minerals; (2) isotope exchange with the water of crystallization; (3) mixing with evaporating waters; (4) mixing with connate waters; and (5) evaporation at the sampling site. The dissolution may cause only a slight shift, as it can easily be seen from an example given in Appendix 1. The isotope exchange is probably the main reason of the shift observed for the 18/III, 19/III, and 5/III leakages, as well as for the N sample (well N_1 – lower layer). This shift should depend on the isotope composition of the water of crystallization and on the fractionation coefficients, which were unknown in the investigated case. The N sample could have been changed only by exchange with the gypsum water. In this case the isotope content of the gypsum water is probably very differentiated since the gypsum cap was formed by waters of different geological ages. Mixing with evaporating waters (from the ponds) almost certainly contributed to the shift, but it cannot be used to explain the shift of the 5/III leakage. Mixing with connate waters should be rejected, as in this case it would be difficult to explain a constant mixing rate. Finally, the evaporation at the sampling site might have contributed to the results from the shafts (strong ventilation).

Leakages from level IX evidently represent connate waters. Two of them (14/IX and 3/IX) showed a tritium content of 8 and 7 TU, respectively. This problem is discussed in more detail in Section 2.

1.5. Some chemical characteristics

Figure 8 shows that all the samples from the Wapno and Kłodawa mines were practically saturated, with the exception of samples from the shafts, well N_1, and those taken at the final stages of flooding. Samples saturated by monovalent salts, when coming into contact with more soluble bivalent salts, become more mineralized at the cost of monovalent salts which are removed from the solution. When water on its way has too short a contact with bivalent salts, then the brine becomes saturated by monovalent salts which are more common (about 98% of NaCl in the Wapno dome). In the case of increasing inflow to the mine, the contact with magnesium salts was evidently too short, and an increase of NaCl content was observed (see Figs 4, 5 and 8). When the contact time is still shorter, the brine samples deviate from the line of saturation (Fig. 8).

From Fig. 8 it is clear that chemical composition of brines cannot serve alone as an indicator of the origin of the brines. Water on its way through a dome may, by dissolution, exchange of salts (Fig. 8), and by mixing with other brines, change its chemical composition to a high degree. Thus, isotope methods seem to be indispensable when investigating the origin of brines, although the isotopic composition of water is also subject to some changes (Fig. 9).

1.6. Artificial tracer experiments

The aim of these investigations was to determine if well N_1 led water from the gypsum salt interface to the leakages of level III. On 23 April 1975, 10 mCi ^{60}Co in the form of $K_3CO(CN)_6$ was injected with 50 g inactive carrier in 6.5 m^3 brine and 20-litre samples were taken from the 18/III and 19/III leakages every three days at the initial stages. After several months the sampling was less frequent (every two weeks). Samples were measured by a 2-inch scintillation probe in a 5-cm lead shield. Because of a high potassium content (see Figs 4 and

5), the detection limit was not better than 0.2 μCi/m^3. Several samples showing a slightly higher activity were checked by a 3-inch scintillation probe with a multi-channel pulse analyser. The increase of activity appeared to be caused by an increase of potassium content. Sampling was ended after 13 months.

On 27 October 1976, 0.6 kg disodium fluorescein (uranin) was injected into well N_1. Samples were taken from the 18/III-2b, 18/III-7 and 19/III leakages every day and, after three weeks, every two or three days. Samples were measured with the aid of the filter fluorometer (Baird-Atomic). The detection limit in the highly mineralized Wapno brines was 3×10^{-10} g/ml (0.3 mg/m^3), for filters chosen according to Behrens [2]. Until the last day of sampling, i.e. 22 July 1977, no disodium fluorescein was found in the samples, although the injected amount was sufficient to trace 2×10^6 m^3 brine.

In 1976 and 1977 sealing operations were performed in directional wells drilled from level III. The hydraulic connections between one of the wells (14a) and other wells and leakages were investigated with the aid of fluorescent dye tracers. In this case 1.3 kg eosin ($C_{20}H_6O_5Br_4Na_2$) and 0.5 kg rhodamine B were injected into well 14a on 29 June 1977. 0.47 m^3 brine was used for the injection (the dyes were diluted in the first 0.170 m^3). The injection was performed with a flow-rate of about 8 litres/min at a pressure of 40 to 45 atm. Samples were collected every two hours for the first three days, and every six hours for the next three days, and once per day later. Applying filters advised by Behrens [2], it was possible to measure independently eosin and rhodamine B. When they appear simultaneously eosin and uranin are not distinguishable by a filter fluorometer, because their emission spectra are too close. However, it is possible to distinguish them when they appear separately.

Injected eosin appeared at several observation points given in Fig. 1, where the appearance time is also shown. Rhodamine B did not appear. On the eighth day after the injection, a pressure test was performed in well 22. This test caused an outflow of brine with a dye that was visible to the naked eye. The outflow took place in chamber 39 and at level IV. The dye experiment described showed that there was an extensive system of interconnected cracks. A slow movement of the tracer and the adsorption of rhodamine suggest that the system consisted of fine cracks. This dye experiment also showed that some of the fluorescent dyes can be easily used in highly mineralized brines, where the use of other tracers is often troublesome.

2. PRELIMINARY RESULTS OF ISOTOPE INVESTIGATIONS IN THE KŁODAWA MINE

The Kłodawa mine is also situated in a Zechstein salt dome, but its hydrogeological situation is quite different to that described in Section 1.1. The cap of the Kłodawa dome is built of thick impermeable clays, and above the dome there are few sediments of low permeability. Brines in the dome can be only of connate origin or from surrounding formations. The isotope composition of the surrounding waters is not known. However, data reported by Tongiorgi and Dowgiałło [3] suggest that their delta values should be much more negative than those found in the dome. The main chemical components of the mine brines are shown in Fig. 8. In addition, they often contain $AlCl_3$ (up to 40 g/l), H_3BO_3 (up to 2 g/l), Fe_2O_3 (up to 1.5 g/l), and sometimes traces of hydrocarbons or H_2S.

The first attemps to measure the isotope composition of these brines in 1974 and 1975 failed. In 1977 five new samples were collected and measured together with two other samples left after the first trials. The results are shown in Fig. 9. The first number indicates the leakage number, while the second gives the mine level expressed in metres. All the leakages seem to represent connate waters. Evidently there are three groups of results. The most positive values in Fig. 9 should be attributed to waters connate in the sense of the salt formation. Two other groups may be connate in the sense of the dome formation phases. In each phase of the upward movement of a dome, small amounts of water from surrounding formations may become included into the dome. Further investigations are needed to support the above suggestions. The pressures and flow-rates of the leakages decline in time, with the exception of the 7/450 leakage which has existed since 1956 with a pulsed flow-rate of approximately 3 litres/h.

It should be mentioned that all the samples from Kłodawa showed 2 to 10 TU, similar to two samples of connate water in the Wapno mine (see Section 2.4.). Samples from the 60/600 leakage (flow-rate of 0.3 litres/h) showed aven 15 and 16 TU in 1974 and 1975, respectively, and a high ^{14}C content. Later, this leakage disappeared, confirming its connate origin. Two samples chosen at random – samples 7/450 and 75/600 – were checked in the IAEA laboratory. Our measurements yielded 10 ± 1 and 5 ± 1 TU, whereas the IAEA measurements gave 9.3 ± 1 and 3.9 ± 0.5 TU, respectively. Thus, it is evident that the contamination took place before the measuring process. In the cases of low flow-rates the contamination may be explained by a long contact of brine with the mine atmosphere. This contact may take place in cracks (close to the outflow points), on the walls of mine excavations, or in a well if the leakage is through the well. Obviously, the problem of this contamination requires further investigation.

3. ISOTOPE INVESTIGATIONS IN THE WIELICZKA MINE

The salt deposit at Wieliczka has been described in a number of papers (e.g. [4, 5]). It consists of two essential parts – the upper part which is

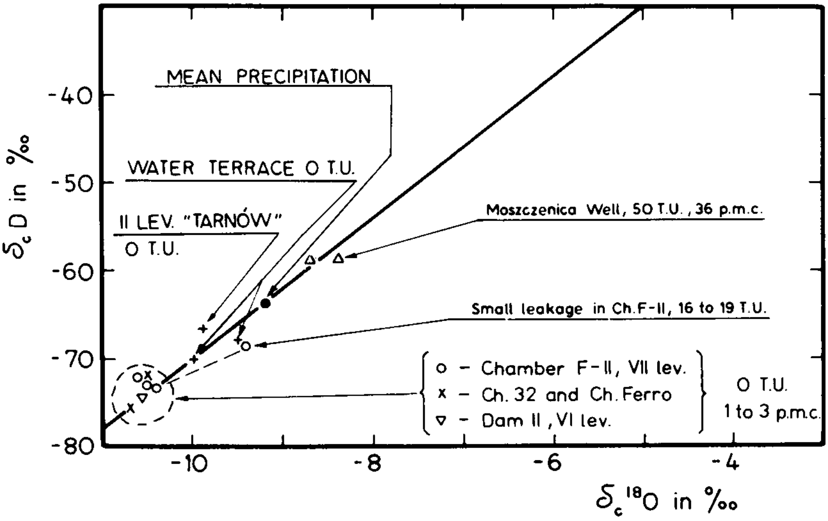

FIG.10. Isotope concentrations of waters in the Wieliczka mine.

developed in the form of coarse breccia composed mainly of salt clays with blocks of salt, which are irregular in shape and vary in thickness, in some places extending to more than 150 m; and the lower part which is developed as a complex of salt layers strongly folded, deformed, and thrust over one another. The salt layers are interbedded with anhydrite and anhydritic clays. In the south, flysch sediments in the form of tongue-shaped wedges are squeezed into the inner part of the salt deposit. Since the salt deposit at Wieliczka has been exploited for about 1000 years, its resources are almost completely exhausted. Present exploitation takes place in the lower part of the deposit, using the system of solution mining in underground boreholes and chambers. In the south the salt deposit is bordered by impermeable flysch formations, and in the north by permeable Chodenice beds. Over the deposit are a weathered gypsum-clay cap and Quaternary loams and sands.

The results of environmental isotope measurements are given in Fig. 10. The precipitation point represents the mean value of shallow groundwaters in the vicinity of Cracow and Wieliczka. It is obvious that all the main leakages to the mine, including the largest one in Chamber F-II (about 20 m^3/h) show waters recharged in a cooler climate no later than about 25 000 years ago. These waters come from the Chodenice beds. Samples taken from the Chodenice beds in well H-8, drilled near the deposit boundary in the vicinity of Chamber F-II, showed the same ^{14}C content and mineralization (about 100 g NaCl per litre) as samples from that chamber.

In 1974 another small leakage (about 0.1 m^3/h) was observed in Chamber F-II. Its mineralization varied between 200 to 300 g NaCl per litre. As can be seen from Fig. 10, this leakage probably originated from another chamber where the water from Chodenice beds was used during exploitation. Its isotope composition might change there by evaporation. The high tritium content was the result of either mixing with surface water that was also used for exploitation work, or molecular exchange between the water in the exploitation chamber and vapour in the mine atmosphere. Later this leakage either disappeared or joined the main leakage, becoming unmeasurable. The isotopic composition of waters from the upper levels of the mine (Water Terrace, Tarnów) suggest that they originate in upper parts of the Chodenice beds. Their ^{14}C content has not yet been measured. These waters were previously thought to be of infiltration origin, as it is known from medieval documents that the water at the Water Terrace was used for mine horses.

The Chodenice beds form a large water reservoir of low permeability (the hydraulic conductivity varies from 10^{-8} to 10^{-6} m/s), which either has no direct hydraulic connections with the infiltration waters, or these connections are far from the mine area. Thus, despite large leakages to the mine, the hydrogeological situation can be considered to be safe, at least as long as the whole system is mechanically stable.

In Fig. 10 an interesting example is also shown from the Moszczenica-Łapczyca deposit [4] situated 20 km from Wieliczka. The well was sampled at a depth of several tens of metres in the gypsum cap. Obviously there was a mixing of young infiltration waters with much older ones. It is quite probable that two types of old waters took part in the mixing. Another deep well (Ł-3) in the area shows the isotopic composition of the exploited brine close to SMOW. This composition should be attributed to original Miocene sea-waters, and is in agreement with the findings of Dowgiałło [6] for other deep Miocene waters in southern Poland.

4. CONCLUSIONS

Investigations performed in three mines and two wells in the area of another deposit show that environmental isotope methods are very useful in identifying the origin of waters occurring in salt mines. The isotopic composition of brine waters has to be expressed both in the activity and in concentration terms, otherwise the interpretation may be hindered. Within this work a tritium contamination of some highly mineralized brines was observed. The mechanism of this effect must be investigated later.

It seems that the isotopic composition of the crystallization water and the fractionation coefficients should also be investigated to clarify the isotopic shift observed for infiltration waters, which are in contact with hydrated salt minerals.

Such investigations should also be helpful in identifying the age of the crystallization of these salts.

Experience gained during this work shows that disodium fluorescein and eosin may be useful as tracers in highly mineralized waters of salt mines.

ACKNOWLEDGEMENTS

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APPENDIX 1

The experimental procedure applied for tritium and ^{14}C determinations was described by Florkowski and Grabczak [7] and Florkowski et al. [8], respectively. Samples of highly mineralized brines were bi-distilled before hydrolysis. After the first distillation they were alkalized, if necessary, by adding Na_2O_2 solution in dead water.

The isotope composition of oxygen was measured as described by Sofer and Gat [9], i.e. the δ_a was determined and the δ_c calculated from graphs given by these authors. These graphs were fully confirmed in control measurements carried out for $CaCl_2$, $MgSO_4$, KCl and NaCl. It was not possible to freeze samples of highly mineralized brines. In such cases the CO_2 was pumped out through a capillary after equilibration.

Pre-distillation of brine samples was also tried. In some cases the proper values of δ_c were observed after the distillation. However, in other cases, the distillation process led to fractionation of ^{18}O. Accidentally, after distillation the brine samples from Wapno and Kłodawa were giving delta values close to the δ_a ^{18}O. Thus, distillation could be used here as a rapid check if the equilibration time was long enough for a given sample. In the case of the samples 7/450, 61/525, 66/525, and 88/600 the applied equilibration time did not appear to be long enough. Therefore, the reported delta values of these samples represent only measurements obtained after distillation. Thus, their accuracy is not very high, but probably no worse than 1‰.

The isotope composition of hydrogen was measured opposite to that way described by Sofer and Gat [10], i.e. δ_cD was measured and δ_aD calculated, using graphs given by these authors. Isotope concentrations were measured after the distillation of samples. Table I gives results showing that the distillation method, applied for solutions of several chosen salts, gives proper δ_c values. In the case of salts such as NaCl and KCl, the standard method, i.e. the reduction to hydrogen gas in a uranium furnace, without prior distillation, also gives δ_c values. Thus, brines containing only NaCl can be measured without distillation.

TABLE I. DETERMINATION OF $\delta_c D$ BY DISTILLATION OF BRINE SAMPLES

Solution	δD (‰)		
	Solvent	Standard measurement	After distillation
KCl (2M)	−78.8 ± 0.3	−80	−79
KCl (4M)		−80	−79
NaCl (2M)		−79	−78
NaCl (4M)		−80	−78
$CaCl_2$ (2M)		−87	−79
$CaCl_2$ (4M)		−86	−79
$CaCl_2$(150 g/l)	−74.5 ± 0.8	−80	−75
$CaCl_2$(150 g/l) + KCl(50 g/l)		−81	−74
$MgSO_4$(150 g/l)	−70.5 ± 0.5	−76	−70
$MgSO_4$(150 g/l) + KCl (50 g/l)		−77	−70

Remark: M = molar concentration, other concentrations being expressed in per litre of solution.

TABLE II. $\delta_c D$ OF BRINE SAMPLES PREPARED FROM CARNALLITE

δD of initial components (‰)		Concentration[a] (g/l)	δD brine (‰)	
Water	Water of crystallization		After distillation	Calculation from initial values
−78.8 ± 0.2	−36.9 ± 0.6	250	−75.7	−75.8 ± 0.2
		400	−75.0	−74.2 ± 0.2

[a] Concentration expressed per litre of solvent.

In Table II another example is given. Here a sample of natural carnallite was used. The $\delta_c D$ values measured and calculated from the composition of initial components are the same within the accuracy of measurements. The isotopic composition of the water obtained after distillation is, of course, shifted in that case because of the dissolving of the hydrated salt. The water content of the carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) used was 80% of the theoretical value.

In Tables I and II standard deviations are given in the cases of repeated measurements. A comparison of the results given by Sofer and Gat [10] in their Fig. 2, with the results presented in Tables I and II, seems to suggest that the method applied here for finding $\delta_c D$ is more accurate than that of the cited authors, at least for the investigated salts. The distillation was performed in small brass vessels under atmospheric pressure. Samples were kept at a temperature of 300°C for five to six hours. Usually the temperature had to be further increased with the aid of a gas burner until complete dryness of the salt samples was obtained.

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DISCUSSION

D.B. SMITH: Was the sensitivity of detection of eosin and rhodamine B such that you could say with certainty that the rhodamine was absorbed?

A. ZUBER: The detection limit of rhodamine (about 10^{-10} g/ml) was better than that of eosin (about 5×10^{-10} g/ml).

D.B. SMITH: Did you change from using ^{60}Co to dyes because of their sensitivity or because the use of dyes was more appropriate for other reasons?

A. ZUBER: We changed to the dye for both the reasons you mention. I would like to add that in laboratory experiments we found a delay with the disodium salt of fluorescein of the order of 30% (factor of 1.3) and an even