RADIOLYTICAL GAS PRODUCTION OF ROCK SALT AFTER IRRADIATION WITH Co-60 SOURCES: POTASAS DEL LLOBREGAT SAMPLES

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ABSTRACT

The production of gas resulting from exposure of rock salt to gamma irradiation has been studied. In order to discern which gases come from radiolysis and which are related to thermal desorption, two sets of experiments were conducted. The first set of experiments consisted of laboratory degasification tests at 50°C, and the second consisted of irradiations using Co^{60} sources at the same temperature. CO_2, H_2, NO_x, SO_x, O_2, CH_4 and chlorine-bearing gases were determined. The obtained results, allowed us to identify gases arising from the radiolysis of organic matter and brine, and also those arising from radiolytical oxidation. In addition, certain amounts of the produced chlorine-bearing gases were trapped inside the halite crystals.

1.   INTRODUCTION

After the disposal of radioactive waste in rock salt, the waste acts as a source of heat and radiation. The emplacement of waste gives rise to a temporary local heating (the first 10 years) and a long lasting general heating of the surrounding rock salt (about the first 1000 years). As a result of the high temperature, primary gases and gases generated by the thermal decomposition of the organic matter are released. In addition to the effect of temperature, gamma-radiation will be responsible for the generation of radiation induced defects in the NaCl crystal and the production of radiolytical gases arising basically from the decomposition of organic matter and brine.

When NaCl is irradiated, the ionization causes Cl^- ions to be ejected from their normal lattice sites to form interstitial chlorine atoms (H-centre) and empty lattice sites. The empty lattice site traps the electron left behind (F-centre), preserving the neutrality of the crystal. At temperatures higher than 30 °C, as is the case of heat producing waste, the primary defects are very mobile due to thermal diffusion (Hodgson et al., 1979). The H-centres are easily trapped in the vicinity of dislocation lines, where molecular chlorine is

formed. In addition, the F-centres can react with Na^+ to form metallic sodium. These metallic sodium atoms tend to form clusters of colloidal size (known as colloidal sodium).

Gamma irradiation also causes decomposition of the organic matter present in the rock salt and radiolysis of brine, which leads to the formation of H_2, H_2O_2 and ClO^- species (Jenks et al., 1975).

The importance of the study of radiolytical gas formation is justified by its impact on the operational phase of the storage facility and on the long term safety. The main effects to be taken into account are: pressure build up in the repository, formation of a corrosive atmosphere, generation of explosive and toxic gas mixtures, and changes in the Eh/pH of brines.

The work reported here is complementary to other studies carried out by other partners (ANDRA and GSF) of the HAW project. (Palut et al., 1993; Jockwer, in press)

2.   EXPERIMENTAL PROCEDURES

The starting material for the irradiation experiments is natural rock salt from the Potasas del Llobregat Mine. Before the irradiation experiments, the water content and the chemical composition were analyzed.

The water content of the starting material was determined by thermogravimetry, and the mineralogical composition was quantified from chemical analysis. Chlorides were determined volumetrically (Mohr method), sulphates determined by ICP-AES (inductively coupled plasma atomic emission spectrometry), and the insoluble fraction calculated gravimetrically (Huertas et al., 1992). In order to determine the amount of organic matter, Total Organic Carbon (TOC) measurements were perfomed in a TOC analyzer (dilution 1:3000). Quantification was performed through peak area integration using the external standard method (the standard concentrations ranged between 2 and 5 ppm of potassium hydrogen phthalate).

The effect of the generation of radiolytical gases was tested in pure and impure rock salt. Crushed salt samples (125g, size < 1 cm), were placed in borosilicate ampoules using natural air as atmosphere, which were then sealed. The volume ratio between salt and air equaled 1. In order to determine the effect of irradiation on the brine, 200 ml of synthetic brine representative of the starting material (Na 2.91 M, Mg 1.15 M, K 0.31 M, SO_4 0.07 M

and Cl 5.40 M) was also placed in two ampoules. One ampoule of air was also irradiated to be used as blank.

Since most gamma radiation energy is converted into heat, two sets of experiments were performed. Duplicate samples were used in both sets of experiments in order to discern which gases were due to the thermal effect and which to radiolysis. The first set of experiments consisted of two laboratory degasification tests carried out in an oven at a constant temperature of 50°C. The first test took 17 hours and the second took 34 hours. The second set of experiments consisted of two irradiations performed in the industrial irradiator CESAR located at Granollers (Spain). This facility operates with Co^{60} sources. In the first irradiation experiment (17 hours) samples received a total dose of 500 kGy, and in the second (34 hours) the dose was 1 MGy . The irradiation conditions for both experiments were: dose rate about 30 KGy/h and temperature from 20° up to 50°C.

Gases were analyzed by gas chromatography (H_2, CO_2, O_2 and light hydrocarbons) and ion chromatography (chlorine-bearing, NO_x and SO_x gases). H_2, CO_2, O_2 and hydrocarbons were quantified by gas chromatography through peak area integration using the external standard method. Samples and standards were injected repeatedly until less than 5% dispersion in the area measurement was observed. The analytical conditions were:

For H_2 and O_2 analysis: Molecular Sieve 5A 80/100 mesh, 3m 1/8" OD; 60°C hold; Carrier gas: Ar, Detector: Thermal Conductivity (TCD).
For CO_2 and light hydrocarbons analysis: Porapak Q 50/80 mesh, 4m 1/4" OD; 120°C hold; Carrier gas: He, Detector: Thermal Conductivity (TCD).

Gas determination by ion chromatography was carried out after dissolving 10 ml of gas sample in 2 ml of a basic aqueous solution (1 mM NaOH). Ionic species were quantified through IC profiles using the external standard method (the standard concentrations ranged between 0.5 and 10 ppm of Cl^-, SO_4^{2-}, NO_2^- and NO_3^-).

In order to determine whether chlorine-bearing gases were trapped in the rock salt, samples were ring milled, and a gas sample was extracted through a septum placed on the mill lid. In addition, the amount of colloidal sodium was determined in order to check the mass balances between chlorine-bearing gases and colloidal sodium. Colloidal sodium was quantified by monitoring the release of H_2, after dissolution of 150 mg of irradiated rock salt in 1.5 ml double-distilled water. The reaction, which is shown in equation [1], took place in a glass vial (V= 5 ml) which was closed with an open-hole screw-cap and a septum. The analysis of H_2 was performed as described above.

$$Na^o + H_2O \longrightarrow 1/2\ H_2 + NaOH \qquad [1]$$
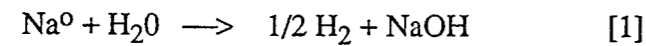
The pH of the brines was measured by a combined glass electrode, and the redox potential of the brines was monitored by means of a platinum wire using that of the combined glass electrodes as a reference (Casas *et al.*, 1992).

3.   RESULTS

The results of the geochemical characterization of the studied rock salt are listed in Table 1. These samples were used as starting material for the thermal degasification and radiolytical gas production experiments.

3.1   Thermally induced degasification of rock salt

The gases released by thermal degasification are listed in Table 2. The results show that besides O_2 (present in the gas atmosphere during the test), CO_2 and CH_4 are also present. Similar results were found in other degasification tests performed in the same rock salt formation (see article 8 of this volume).

The amount of CO_2 is not time dependent, suggesting that its desorption takes place during the first few hours after heating. Impure rock salt contains slightly higher amounts of CO_2 than pure rock salt.

The presence of CH_4 is also associated with the impure rock salt. A relationship between the measured amounts of CH_4 and the potential amount of thermally releaseable gases (mainly CH_4) arising from the decomposition of the organic matter present in the rock, is not apparent. The low contents of measured CH_4 suggests that thermal decomposition of the organic matter has not still taken place at this temperature. Moreover, the desorption of CH_4 is not time dependent since it took place at the early stages of the experiment. The presence of H_2, when compared with results of previous experiments (see article 8 in this volume), could be explained by the fact that the concentration in the gas phase was increased by lowering the volumetric ratio between atmosphere and rock salt sample.

Table 1: Chemical composition of Potasas del Llobregat samples used in the degasification experiments.

SAMPLE	HALITE %	ANHYDRITE %	CLAY %	IG. BRINE %	F.I %	TOC ppm
11	98.32	1.66	0.12	0.12	0.14	43
12	98.61	1.20	0.19	0.09	0.07	105
41	87.44	11.94	0.64	0.23	0.15	122
42	98.90	1.02	0.08	0.06	0.29	78

Note: IG.brine stands for intergranular brine, F.I for fluid inclusions and TOC for total organic carbon content.

Table 2: Thermally induced (50°C) degasification experiment.

SAMPLE	HEATING PERIOD hours	H_2 μg/kg	CO_2 mg/kg	O_2 ml/l	CH_4 mg/kg	NO_x ml/l	SO_x mg/kg
11	17	13	3.6	55	tr	n.d	n.d
11	34	9	3.7	64	n.d	n.d	n.d
12	17	tr	1.4	59	n.d	n.d	n.d
12	34	32	4.4	61	n.d	n.d	n.d
41	17	70	4.3	61	0.2	n.d	n.d
41	34	21	4.1	62	tr	n.d	n.d
42	17	7	3.7	61	n.d	n.d	n.d
42	34	38	3.7	65	n.d	n.d	n.d

Note: Gas content of H_2, CO_2 and SO_x are expressed as mg or μg per kg rock salt. Gas content of O_2 and NO_x are expressed as ml/litre in the gas phase.; n.d = not detected; tr = trace (about 1 μg/kg in the case of H_2 and 10 μg/kg in the case of CH_4).

Table 3: Laboratory degasification experiment of samples subjected to heat (50°C) and gamma radiation.

SAMPLE	DOSE kGy	H_2 μg/kg	CO_2 mg/kg	O_2 ml/l	Cl mg/kg	NO_x μl/l	SO_x mg/kg
11	500	33	3.4	57	---	---	---
11	1000	45	4.6	44	2.2	0.4	1.96
12	500	63	4.1	44	0.6	0.8	0.31
12	1000	60	5.2	56	2.2	2.4	0.80
41	500	145	3.8	56	---	---	---
41	1000	157	4.9	34	1.2	1.4	0.61
42	500	47	3.2	33	0.4	tr	0.45
42	1000	23	5.1	59	0.9	0.4	1.90
BRINE	500	4000	1.2	52	---	---	---
BRINE	1000	5700	---	48	0.04	1.3	0.35
AIR	1000	5	1.1	48	---	---	---

Note: Gas content of H_2, CO_2, Cl and SO_x in rock salt samples are expressed as mg or μg per kg, whereas in brine and air are expressed as mg or μg per litre brine or air respectively. Gas content of O_2 and NO_x are expressed as ml or μl per litre in the gas phase. --- = not analyzed.

Table 4: Comparison between the measured and calculated $G(H_2)$ values.

SAMPLE	DOSE kGy	H_2 μg/kg	IG %	G meas.	G calc.
11	500	33	0.12	0.0140	0.0011
11	1000	45	0.12	0.0098	0.0008
12	500	63	0.19	0.0202	0.0017
12	1000	60	0.19	0.0153	0.0012
41	500	145	0.23	0.0428	0.0021
41	1000	157	0.23	0.0336	0.0015
42	500	47	0.06	0.0061	0.0005
42	1000	23	0.06	0.0049	0.0004

Note: H_2 values expressed as μg H_2 for Kg rock salt and IG stands for intergranular brine and is expressed in % weight. G meas. stands for measured $G(H_2)$ value, whereas G calc. stands for calculated $G(H_2)$ value. The calculated $G(H_2)$ value is computed by multiplying the amount of intergranular brine by the experimental $G(H_2)$ values for brines. $G(H_2)$ value for a dose of 500 kGy equals 0.92, whereas $G(H_2)$ value for a dose of 1 MGy equals 0.65.

3.2 Gas generation due to the combined effect of heat and gamma radiation on rock salt

The gases released in the irradiation experiments are listed in Table 3. It is noticeable that CO_2 increases with irradiation time. Nevertheless, most of the CO_2 released is related to thermal desorption, and only minor amounts are attributable to radiolysis. CH_4 was not detected in samples that had been subjected to radiolysis, in contrast to their equivalents that were subjected to heating experiments. The absence of CH_4 in the irradiated samples could be explained by reaction with O_2, which would produce CO_2 and H_2 under gamma ray exposure, as proposed by Bonne et al. (1980) in equivalent experiments in Boom clay samples, which are enriched in hydrocarbons.

The radiolytic yield (G) for H_2 production arising from the radiolysis of water and brines has been extensively studied in a variety of experimental conditions (Brewitz and Mönig, 1992; De Canniere et al., 1992). The G-value is the number of gas molecules generated per 100 eV. The G-values for H_2 production in irradiated brines vary between 0.45 and 2.1 (Brewitz and Mönig, 1992), whereas in aqueous-like solutions (De Canniere et al., 1992) they range between 0.65 (for a dose of 210 kGy) to 0.25 (for a dose of 13500 kGy). The G-values obtained for the brines studied in our experiments are 0.92 for a dose of 500 kGy and 0.65 for a dose of 1 MGy. The G-values obtained empirically in the studied salt samples and those expected taking into account their intergranular water content, are given in Table 4. The measured G-values are higher than the expected, suggesting that part of the H_2 is from other sources.

While the radiolysis of brines has been studied extensively, the multicomponent system reactions of the gas phase are not so clear. The production of CO_2 and H_2 from the recombination of CH_4 and O_2, cannot be explained from the obtained results. An additional source of CH_4 may be involved, which could be the degradation of the organic matter induced by irradiation. Moreover, there is a depletion of O_2 in some of the samples, which supports the hypothesis that CH_4 can be generated when sufficient organic matter is present in the rock salt under oxidizing conditions.

The production of H_2 depends on dose and, as pointed out above, on the amount of water, organic matter and CH_4 present in the rock salt. NO_x is an irradiation product of air (Palut et al, 1993) which increases with increasing dose. The amount of chlorine-bearing gases (probably Cl_2 and $HCl_{(g)}$; Brewitz and Mönig, 1992) increases with dose and is of the same order of magnitude as the amount of colloidal sodium. The amount of SO_x also increases with the dose, which cannot be explained yet, since it is not related to the amount of

sulphatic minerals present in the rock salt.

The effect of irradiation on the brine has also been studied, since changes in brine properties (Eh and pH among other parameter) affect either the UO_2 or the glass matrices dissolution rate (Grambow, 1990). The initial conditions of the brine, in the presence of air before irradiation, were pH 6.0 and Eh 530 mV. After irradiation, the pH and Eh dropped to 5.6 and to 310 mV and to 4.2 and 430 mV for 500 kGy and 1 MGy respectively. This change of Eh and pH can be relevant, since acidic and oxidizing conditions enhance the liberation of radionuclides.

The amount of colloidal sodium ranges between 3.5 and 4.9 * 10^{-6} mol for a dose of 500 kGy and between 5.7 and 6.8 * 10^{-6} mol for a dose of 1 MGy. Assuming that chlorine-bearing gases are present in form of Cl_2, the molar fractions obtained would range between 6.1 * 10^{-7} and 1.0 *10^{-6} mol for a dose of 500 kGy and between 1.4 and 3.6 * 10^{-6} mol for a dose of 1 MGy. The $Cl_2/2Na^o$ ratio in the studied samples was always below 0.2, suggesting that important amounts of Cl_2 may be produced but trapped inside the halite crystals. In order to verify this hypothesis, chlorine-bearing gases present in the irradiated rock salt were determined. Their concentration in the rock salt ranged between 4.6 and 9.8 * 10^{-6} mol (for a dose of 1 MGy), which represent between 60 and 70 % of the produced chlorine-bearing gases. These results confirm that the major part of chlorine-bearing gases are trapped in the rock salt.

4. CONCLUSIONS

Since in irradiation experiments rock salt is subjected to the combined effect of heat and gamma radiation, the key to understanding the generation of radiolytic gases lies in performing duplicate experiments in the same samples subjected only to heat. The experiments reported here, have allowed us to recognize the gases released thermally and those which arise from the direct radiolysis of brine, mineral phases and organic matter present in the rock salt studied. Moreover, it has been shown that a third source of gas production is related to complex interactions of the multicomponent system of the gas phase.

Regarding the gases released by heating, besides the presence of oxygen attributed to the use of natural air as atmosphere in the experiments, degasification of rock salt leads to influx of CO_2, and minor contents of CH_4 and H_2 to the gas phase. There is a relationship between the mineralogical composition of the rock salt and the amount of CO_2 and CH_4. On the other hand no relationship was found between the amount of CH_4 and the amount of

organic matter contained in the sample. This observation supports the hypothesis that thermal decomposition of the organic matter takes place at temperatures higher than 50°C.

In the case of the degasification of rock salt subjected to heat and gamma radiation, the production of CO_2, H_2, NO_x, chlorine-bearing gases and SO_x increases with the dose absorbed. However, CH_4 is absent and the amount of O_2 is lower in some of the irradiated and heated sample than in only heated samples. The relationship between mineralogical composition of the rock salt and gas yields, which was found in the experiments where the samples were only heated, cannot be extrapolated to the samples subjected to the combined effect of heat and gamma radiation experiments.

NO_x is an irradiation product of air, whereas the presence of SO_x is not fully understood. The amount of chlorine-bearing gases is of the same order of magnitude as the concentration of colloidal sodium. However, the ratio $Cl_2/2Na^o$ is below 0.2, which suggests that part of the Cl_2 is trapped in the halite crystals. The trapping of chlorine-bearing gases in the NaCl lattice has furthermore been confirmed by gas analysis of ground rock salt, where the additional chlorine-bearing gases (ratio about 0.6) make the $Cl_2/2Na^o$ closer to 1. This phenomenon would minimize the output of chlorine-bearing gases through the repository.

Besides the production of H_2 due to radiolysis of H_2O, minor amounts of chlorine-bearing gases are formed in the brine radiolysis experiments. Furthermore, the hypothetical presence of oxidizing species in solution such as H_2O_2 and ClO^- could be responsible for Eh and pH changes in the brine. The initial conditions of pH of 6.0 and Eh of 530 mV dropped to 5.6 and to 310 mV and to 4.2 and 430 mV for 500 kGy and 1 MGy respectively. This change of Eh and pH of the brine due to radiolysis can be relevant, since acidic and oxidizing conditions enhance the liberation of radionuclides.

Comparison of both sets of experiments (not irradiated and irradiated) suggests that irradiation favours the production of CO_2 and H_2 from the recombination of CH_4 with O_2. However, the results indicate that not all the CO_2 and H_2 can be attributed to the combined action of direct radiolysis of the brine and radiolytic oxidation of CH_4. It is therefore inferred that an additional source of CH_4 might have been present, which probably consisted of the organic matter present in the samples.

The obtained results show that small amounts of corrosive, toxic and explosive gases will be formed by heating and/or gamma irradiation of rock salt. The amount of the gases produced by irradiation (NO_x, SO_x, H_2 and chlorine-bearing gases) will depend on dose and temperature, and probably will affect only the engineering barrier made of salt backfill.

Moreover, brine will become more acidic and oxidized, enhancing the liberation of radionuclides. Furthermore, the amount of gases derived from thermal degasification (mainly CO_2 and CH_4) is not time dependent and may reach its saturation level at early stages of waste emplacement. Finally, the effect of pressure build-up due to the presence of gases of all origins (overpressure in the glass container was noticed after the experiments), could be minimized by proper design of long-term seals in the repository concept.

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