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H_2 and Cl_2 Production in the Radiolysis of Calcium and Magnesium Chlorides and Hydroxides

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The production of H_2 has been examined in the γ-ray and 5 MeV He ion radiolysis of $CaCl_2{\cdot}2H_2O$, $CaCl_2{\cdot}6H_2O$, $Ca(OH)_2$, $MgCl_2{\cdot}2H_2O$, $MgCl_2{\cdot}6H_2O$, and $Mg(OH)_2$. The highest yield for the formation of H_2 is observed in the γ-radiolysis of $MgCl_2{\cdot}2H_2O$ (0.72 molecule/(100 eV), 75 nmol/J), but the yield decreases with dose due to the relative instability of the dihydrate. The H_2 yields with the other compounds range from 0.04 to 0.2 molecule/(100 eV) (4.2−21 nmol/J), which is lower than that from pure water or 2 M chloride solutions. There appears to be no relationship between the results for H_2 from waters of hydration with that from aqueous salt brines. No particular trend is observed in the radiation chemical yields of H_2 with respect to the cation or the degree of hydration. The production of Cl_2 is found only in the γ-radiolysis of $CaCl_2$ with a few weight percent of excess water. No Cl_2 was found in the 5 MeV He ion radiolysis of identical systems. None of the other compounds examined here showed detectable amounts of Cl_2 formation.

Introduction

Very little information exists on the nature of the stable chemical products produced by the passage of ionizing radiation in solid chloride salts despite the importance of these materials in the storage of radioactive materials. Solid-state radiolytic effects such as the production of F, H, or V centers have long been examined in a number of chloride salts, especially NaCl.[1,2] A variety of studies have also been performed on salt brines, but as shown later there is very little relationship between the radiation chemistry of brine and a solid salt.[3−15] Pyrochemical processing of plutonium in chloride salt media has been proceeding for many decades. Significant amounts of plutonium-containing materials have accumulated that are often associated with large quantities of potassium, sodium, magnesium, and calcium chloride salts.[16−18] Salt content can be from about 8 to 20 wt %, depending on the degree of calcination. Self-radiolysis of radioactive processed material in storage can lead to the production of H_2 from moisture, which is an important explosion hazard, and Cl_2, which can be converted to HCl giving a corrosion potential. Chloride attack on metal storage containers is well-documented.[19−22] The production of gaseous products such as H_2 and Cl_2 is especially important in the storage of processed nuclear materials such as plutonium, which must be stabilized, packaged, and stored for up to 50 years in sealed containers.[18] This issue will also be important for the storage of nuclear waste in geologic salt repositories such as the Waste Isolation Pilot Plant (WIPP), USA, and Gorleben, Germany.

The solid-state effects due to the radiolysis of sodium chloride have been fairly well-characterized, and similar results are expected in the magnesium and calcium chlorides. The main effects of concern to the radiolytic formation of H_2 and Cl_2 are the formation of centers (F, V, and H, etc.); generation and trapping of elemental chlorine in the salt; storage and release of energy; and saturation and annealing effects.[1,2] Highly colored F centers are formed when electrons produced by the irradiation are trapped in chloride vacancies.[23] Less than 0.1% of electrons are expected to be trapped in this manner.[24] F centers are thought to be the source of H_2 observed on dissolving NaCl in water following irradiation.[25,26] Hydrated electrons, a potential source of H_2, have also been observed when irradiated NaCl is dissolved in water.[27] H_2 production following salt solvation is accomplished by the transfer of an energetic species from the solid salt to the water. Similar processes may occur when water is associated with the chloride as in the case of waters of hydration.

H centers are formed when electrons are stripped from the chloride anions to give radicals that then diffuse to form molecular chlorine anions trapped at interstitial sites.[2] Several studies have tried to measure Cl_2 production because of its immense corrosive potential. Minute amounts of Cl_2 has been detected in the radiolysis of NaCl to very high ($>10^7$ Gy) doses.[28] Other studies irradiated NaCl or $MgCl_2{\cdot}6H_2O$ to 7 MGy, dissolved them in water, and searched for hypochlorite.[29] Cl_2 formation was suggested, but no accurate quantitative measurements were made. Monitoring the headspace with a mass spectrometer during the radiolysis of solid NaCl again suggested the presence of Cl_2, but without quantitative measurement.[30] Cl_2^- was observed in radiolysis of concentrated $MgCl_2$ aqueous solutions.[31] No consensus on the formation or yield of Cl_2 in the radiolysis of solid chloride salts has emerged. On the other hand, excellent spectroscopic studies have been performed recently on various chlorine species following the radiolysis of aqueous solutions of NaCl, $MgCl_2$, and multicomponent brines.[15,32] The formation of chlorine species may lead to the oxidation of actinide species (Pu, Am, Cm, Np, and U) to higher oxidation states if they are present.[10,33]

In this work, the formation of gaseous H_2 from the radiolysis of $CaCl_2{\cdot}2H_2O$, $CaCl_2{\cdot}6H_2O$, $MgCl_2{\cdot}2H_2O$, and $MgCl_2{\cdot}6H_2O$ was examined. Cl_2 formation from the hydrated, anhydrous, and wet calcium and magnesium chlorides was also examined. The irradiations were performed with both γ-rays and 5 MeV helium

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ions (α-particles) in order to examine the effect due to the linear energy transfer (LET = stopping power, $-dE/dx$) of the radiation and to mimic the conditions in mixed storage with high concentration of γ-emitting actinides (Am, Np, etc.) along with α-emitting actinides such as Pu, Am, and U, etc. Calcination of the chlorides is expected to reduce the chlorides to the oxides.[18,34] The presence of water can then form hydroxides. For this reason, H_2 production was examined in the γ-ray and 5 MeV helium ion radiolysis of $Mg(OH)_2$ and $Ca(OH)_2$ powders. The experiments give fundamental knowledge related to the mechanism for the formation of H_2 from hydroxides and from waters of hydration and provide useful information for the management of packaged nuclear materials and waste.

Experimental Section

The salts used in this work were as follows: calcium chloride anhydrous, $CaCl_2$ (Alfa Aesar, ACS grade); calcium chloride dihydrate, $CaCl_2{\cdot}2H_2O$ (Aldrich, 99.99%); calcium chloride hexahydrate, $CaCl_2{\cdot}6H_2O$ (Aldrich, 98%); calcium oxide, CaO (Aldrich, 99.995%); calcium hydroxide, $Ca(OH)_2$ (Aldrich, 99.995%); magnesium chloride anhydrous, $MgCl_2$ (Alfa Aesar, ACS grade); magnesium chloride hexahydrate, $MgCl_2{\cdot}6H_2O$ (Aldrich, 99.99%); magnesium oxide, MgO (Aldrich, 99.99%); and magnesium hydroxide, $Mg(OH)_2$ (Alfa Aesar) powders. The oxides, hydroxides, and anhydrous chlorides were baked at 100 °C for 24 h to remove adsorbed water. No major changes in these compounds occur under this drying condition as suggested by the relatively small weight changes. The hydrates were dried under vacuum at room temperature or in a drybox with Drierite (calcium sulfate). No difference in the two drying techniques was observed. Variation in weight was used to confirm that only excess water was removed and not waters of hydration. Drying the hydrates at temperatures of 100 °C often resulted in the loss of waters of hydration. Magnesium chloride dihydrate, $MgCl_2{\cdot}2H_2O$, was made by baking the hexahydrate at 100 °C under vacuum. The change in weight corresponds to formation of the dihydrate. Furthermore, the dried compound dissolves in water, whereas magnesium oxide does not.

The heavy ion radiolysis experiments were performed using the facilities of the Nuclear Structure Laboratory of the University of Notre Dame Physics Department. ^4He ions were produced and accelerated using a 10 MV FN Tandem Van de Graaff. After acceleration, the ions were energy and charge-state selected magnetically. The window assembly was the same as reported earlier and gave a beam diameter of 6.4 mm with a uniform flux across the sample surface.[35,36] Energy loss of the helium ions in passing through all windows was determined from a standard stopping power compilation.[37] The samples were irradiated with completely stripped ions at a charge beam current of about 1.5 nA. Absolute dosimetry was obtained from the product of the integrated beam current and the particle energy. The ranges of the helium ions are smaller than the sample thickness, so the ions are completely stopped in the sample and the radiation chemical yields represent all processes from the initial particle energy to zero and are therefore track-averaged yields. The sample cell ($\phi \sim 1$ cm, $L \sim 0.3$ cm) was made of quartz with a thin ($\sim$4−6 mg/cm^2) mica window epoxied to the front for the beam entrance. Inlet and outlet ports allowed the cell to be purged before and after the irradiation. Irradiations were performed at room temperature (23 °C), and the dose rate was sufficiently small that no significant macroscopic heating was observed; see below.

Radiolysis with γ-rays was performed using a Shepherd 109 ^{60}Co source at the Radiation Laboratory of the University of Notre Dame. The dose rate was 150 Gy/min, as determined using the Fricke dosimeter.[38] The sample cell was made from a quartz cuvette with inlet and outlet ports for purging the sample before and after irradiation. The same cuvette was used for both dosimetry and sample irradiation. The ambient temperature of the irradiation chamber was about 30 °C, and samples would rise to this temperature during long irradiations.

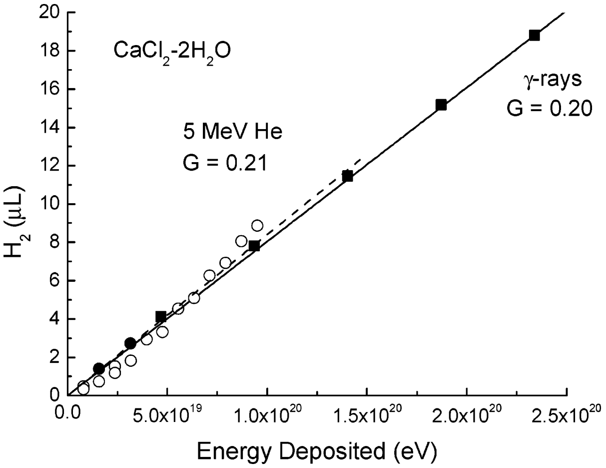

Figure 1. Dose dependence of H_2 production in the radiolysis of $CaCl_2{\cdot}2H_2O$: (■) γ-rays; (○, ●) 5 MeV ^4He ions. The slopes of the fitted lines correspond to *G*-values of 0.20 and 0.21 molecule/(100 eV), respectively.

Hydrogen was determined using an inline technique with a gas chromatograph. Ultrahigh purity argon was used as the carrier gas with a flow rate of about 50 mL/min. The argon passed through a constant flow regulator, an injection septum, and a four-way valve and into a 3 m 5× molecular sieve column of an SRI 8610C gas chromatograph with a thermal conductivity detector. Calibration of the detector was performed by injecting pure gases with a gastight microliter syringe. The sample cell was connected to the gas analysis system using the four-way valve, which was used to purge the sample and then isolate it during irradiation. Following the irradiation, the four-way valve was opened and the radiolytic gases analyzed. Estimated error in gas measurements is estimated to be about 10%.

Samples for molecular chlorine determination from γ-radiolysis were placed in Pyrex tubes ($\phi \sim 1$ cm, $L \sim 10$ cm), purged with argon, and heat-sealed. Following irradiation the tubes were broken, the solid mixed with water, and Cl_2 determined by the DPD colorimetric technique, EPA Method 330.5, using a Chemetrics I-2001 analytical kit.[39] This technique involves the hydrolysis of Cl_2 to the hypochlorite ion or hypochlorous acid followed by reaction with KI at pH 4 or less to give iodine. Iodine reacts with *N*,*N*-diethyl-*p*-phenylenediamine, DPD, to give a red color with two wide absorption bands at 510 and 550 nm. Calibration was performed with known NIST traceable Cl_2 standards. Error in Cl_2 determination is estimated to be 10%. Helium ion radiolysis was performed in cells similar to that used for H_2 measurements, and following irradiation the sample was transferred to a closed vessel containing water.

Results and Discussion

H_2 Production from Calcium Compounds. H_2 production in the radiolysis of $CaCl_2{\cdot}2H_2O$ and $Ca(OH)_2$ with both γ-rays and 5 MeV helium ions gave linear responses as a function of total adsorbed dose. A typical response for $CaCl_2{\cdot}2H_2O$ is shown in Figure 1. The slopes of the dose responses shown in Figure 1 are proportional to the radiation chemical yields, or *G*-values.

TABLE 1: Radiolytic Yields of H_2 with γ-rays and 5 MeV He Ions[a]

	γ-rays	5 MeV He
$CaCl_2{\cdot}2H_2O$	0.20	0.21
$CaCl_2{\cdot}6H_2O$	0.098	0.038
2 M $CaCl_2$	0.49	0.77
$Ca(OH)_2$	0.20	0.051
$MgCl_2{\cdot}2H_2O$	0.72 (0.51)[c]	0.38 (0.22)[c]
$MgCl_2{\cdot}6H_2O$	0.042	0.14
$Mg(OH)_2$	0.051	0.038
2 M $MgCl_2$	0.56	1.34
CeO_2[b]	0.018	0.018
ZrO_2[b]	0.08	0.018
UO_2[b]	0.018	0.018

[a] In units of molecule per 100 eV. [b] With 1 wt % water adsorbed.[29,30] [c] High-dose yield in parentheses.

Radiation chemical yields are traditionally given in units of molecules of product per 100 eV of total energy deposited in the medium. The *G*-values reported here for helium ions are track-averaged yields since the ions are completely stopped in the sample. Figure 1 shows that the radiation chemical yields of H_2 from $CaCl_2{\cdot}2H_2O$ are nearly the same (~0.2 molecule/(100 eV)) for both γ-rays and 5 MeV helium ions. A similar value is observed in the γ-radiolysis of $Ca(OH)_2$, as shown in Table 1. The 5 MeV He ion radiolysis of $Ca(OH)_2$ gives a significantly lower yield (~0.05 molecule/(100 eV)). Linear responses to dose are observed for both of these compounds with both types of radiation, indicating straightforward radiolytic processes are responsible for H_2 production.

The yield of H_2 in the radiolysis of water is about 0.45 molecule/(100 eV) and mainly due to reactions of the hydrated electron or its precursor.[40] H_2 yields in the radiolysis $CaCl_2{\cdot}2H_2O$ are about half of this value, indicating the compound readily decomposes to give H_2. Ionizing radiation deposits energy to the electrons of a medium so most of the initial energy loss is to the $CaCl_2$ moiety. Presumably energy is transferred to the water resulting in the formation of the oxide or hydroxide, but no specific analysis was performed. H_2 yields with the 5 MeV He ion radiolysis of $Ca(OH)_2$ are lower than that observed with γ-rays even though samples were irradiated under identical conditions. There is no reason to assume that the decomposition of $Ca(OH)_2$ in helium ion radiolysis is less than in γ-radiolysis, so radical or other reactive precursors to H_2 must be recombining in the high LET helium ion track to give other products. No O_2 was observed in these systems as also suggested in earlier studies by Jenks and Walton.[4]

The γ-radiolysis of $CaCl_2{\cdot}6H_2O$ is complicated by heating of the sample by the source. With long irradiations, the sample temperature increased to that of the γ source, which was about 30 °C. A previous work reports that $CaCl_2{\cdot}6H_2O$ acts like a single compound with a melting point at about 29 °C.[41] The heat capacity of this compound was shown to start rising at about 25 °C, indicating some structural changes occurring at very near room temperature. Short doses with new samples repetitively gave yields of 0.098 and 0.038 molecules of H_2 per 100 eV of energy absorbed for γ-rays and 5 MeV helium ions, respectively. Under longer irradiations, higher doses, the yields in γ-radiolysis increased and approached the yield found with 2 M aqueous solutions. The samples visually appeared to be melted in γ-radiolysis. An increase in H_2 yields could be observed in helium ion radiolysis, especially at higher dose rates. No visual change to the sample was observed in the 5 MeV He radiolysis, but the penetration is only expected to be about 15 μm. The heating of such a small volume would be difficult to observe or measure. Sample heating by the heavy ion irradiation must be due to low-level heating due to the slow transport of heat from the irradiation zone. On the other hand, the 5 MeV He ion radiolysis of $CaCl_2{\cdot}6H_2O$ at higher temperatures is expected to give H_2 yields approaching that observed in 2 M $CaCl_2$ solutions. A temperature of 30 °C is certainly expected in many nuclear material storage conditions, and the variation of H_2 yields as the $CaCl_2{\cdot}6H_2O$ melts is significant.

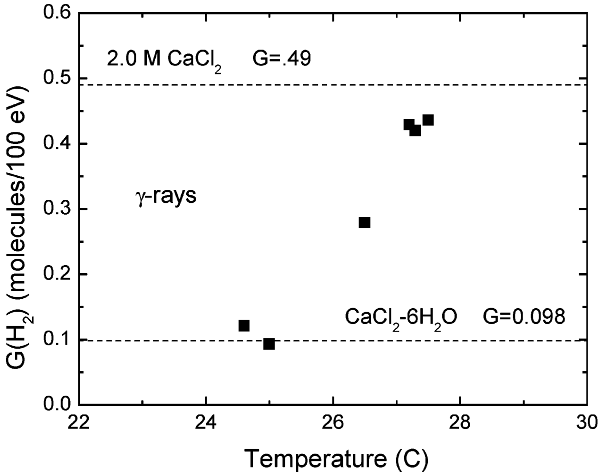

Figure 2. Temperature dependence of H_2 production in the radiolysis of $CaCl_2{\cdot}6H_2O$ with γ-rays. The lower line shows the yield at 22 °C, while the upper line shows the yield in 2 M aqueous $CaCl_2$ solution.

An attempt was made to estimate the relative heating with respect to dose with γ-rays by measuring the temperature rise of the sample, and the results are shown in Figure 2. The lack of good thermal conductivity probably leads to an uneven heating of the sample, so the present method of estimating temperature rise is crude and intended to only show the general increase in H_2 yield as the sample approaches its melting point. An increase in H_2 yield to about 0.57 molecule/(100 eV) was observed in He radiolysis. The variation in H_2 yield between the 2 M solutions and the solid compounds show that data from salt brine studies are not suitable for relatively dry solid salts. This is true although 2 M $MgCl_2$ and 2 M $CaCl_2$ solutions give similar radiation chemical yields of H_2 to those obtained by previous researchers.[4,42] The radiation chemistry of the brines are characterized by the chloride anion reaction with excited water to give H_2.[3-6]

An attempt was made to measure the production of H_2 from CaO and MgO with small amounts of adsorbed water in order to compare with previous results on CeO_2, ZrO_2, and UO_2.[43,44] There is partial or complete conversion of both magnesium and calcium chloride salts to CaO and MgO under some of the conditions associated with plutonium processing for storage.[34,45] The H_2 yields were found to increase with increasing water weight percent for both CaO and MgO powders. However, when these oxides are left for long periods of time in humid conditions they slowly convert to the corresponding hydroxides. Calcium oxide converts to the hydroxide more rapidly than does magnesium oxide, which may be the reason that H_2 yields with $Ca(OH)_2$ are higher than $Mg(OH)_2$.[46] At low water loadings, it could never be ascertained that the oxides had adsorbed water or that a small fraction had simply converted to the hydroxides and the results represented that found with mixtures. Total H_2 yields from CeO_2, ZrO_2, and UO_2 are significantly lower than the hydrates or hydroxides examined here; see Table 1. Hydroxides may have a substantial contribution to H_2 formation in certain waste storage conditions.

H_2 Production from Magnesium Compounds. The production of H_2 in $Mg(OH)_2$ was found to be linear with dose for

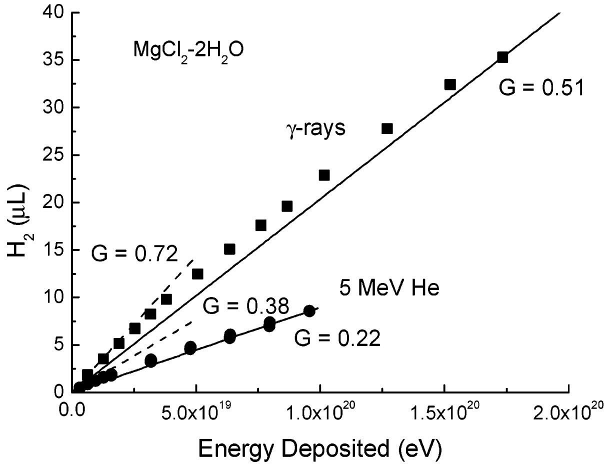

Figure 3. Dose dependence of H_2 production in the radiolysis of $MgCl_2{\cdot}2H_2O$: (■) γ-rays; (●) 5 MeV ^{4}He ions. The dashed lines show the low-dose limiting yields.

both types of irradiation. *G*-values for H_2 of 0.051 and 0.038 molecule/(100 eV) were determined for γ-rays and 5 MeV helium ions, respectively; see Table 1. The yield with 5 MeV He ions is comparable to those found in the radiolysis of $Ca(OH)_2$. However, the H_2 yield in the γ-radiolysis of $Ca(OH)_2$ is considerably greater than that of $Mg(OH)_2$. Previous work has shown that $Mg(OH)_2$ is converted to MgO with radiolysis, but the mechanism is not established.[47] The formation of water may predominate over the production of H_2 in the radiolysis of $Mg(OH)_2$ since MgO is relatively inert.[46]

There is a variation of about a factor of 3 in the H_2 yields between the calcium and magnesium chloride hexahydrates. No obvious trend exists for the yields as a function of cation or radiation type. Even the relative H_2 yields in $CaCl_2{\cdot}6H_2O$ decrease from the γ-radiolysis to the 5 MeV He ion radiolysis, while the inverse is found for $MgCl_2{\cdot}6H_2O$. In many of the solids examined here, the H_2 yield in γ-radiolysis is greater than or equal to that in 5 MeV He radiolysis. This result is very different from that of liquid water or the salt brines, which again shows that the results with salt brines cannot be used to predict the yields in solid salts.

The radiolysis of $MgCl_2{\cdot}2H_2O$ with γ-rays and 5 MeV helium ions exhibit nonlinear responses as a function of dose; see Figure 3. H_2 yields are found to decrease with increasing dose. The *G*-values measured at the lowest doses in this work are 0.72 and 0.38 molecule/(100 eV) for γ-rays and 5 MeV helium ions, respectively. These values decrease to 0.51 and 0.22 molecule/(100 eV), respectively, and may be slowly approaching the yields observed with $MgCl_2{\cdot}6H_2O$ or $Mg(OH)_2$ as the dihydrate decomposes. This finding is similar to an earlier work that suggested heating the samples to liquefaction temperature leads to the release of H_2.[4] All the H_2 yields for $MgCl_2{\cdot}2H_2O$ are high, indicating the relative ease of this system to radiolytically decompose. Hydrogen yields are probably highly dependent on the presence and form of water on the salts, i.e., adsorbed, absorbed, water of hydration, or inclusion fluid and on the storage temperature of the nuclear material.[8,13]

Cl_2 Production from Calcium Compounds. Previous results in the literature are inconclusive in showing the formation of Cl_2 in the radiolysis of chloride salts.[28−33] A trace of gaseous Cl_2 was detected in the radiolysis of NaCl.[30] However, gaseous Cl_2 is extremely reactive, especially with water or metal surfaces, and difficult to observe reliably using gas sampling techniques. HCl may be even more important for corrosion effects. It may also be formed in the radiolysis of these compounds but not detected using the present technique. The present experiments focused on the determination of Cl_2 trapped or otherwise associated with the solid salts. Of course, any loss of Cl_2 to the cell walls or atmosphere will not be observed in the experiments reported here. A further search for Cl_2 will have to be undertaken in which both the solid and gas phases are sampled. The results reported here are meant to be a survey for possible Cl_2 formation in the solid salt.

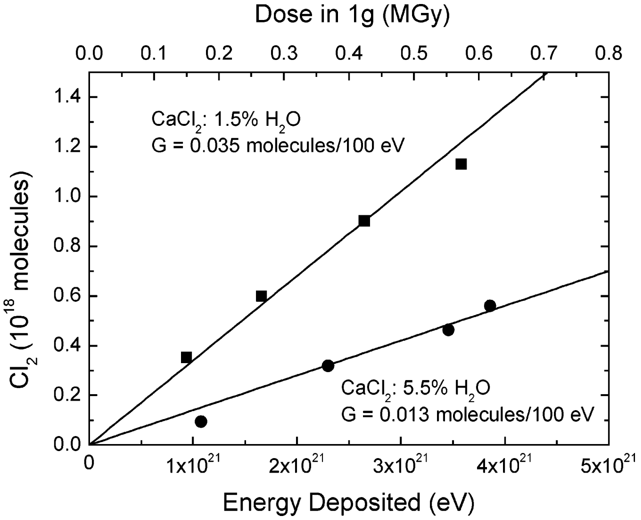

Figure 4. Production of Cl_2 as a function of dose from $CaCl_2$ for various amounts of added water: (■) 1.5 and (●) 5.5 wt % water.

Radiolytic chlorine production was examined for all the chlorides in this work. The salts were either dry or loaded with known amounts of water, irradiated, and then dissolved in water and chlorine determined. Chlorine was never observed in any of the dried salts at doses up to about 1 MGy. This dose corresponds to *G*-values of Cl_2 production in γ-radiolysis of less than 0.002 molecule/(100 eV). Significantly higher doses may lead to observable Cl_2, but those doses are far too large for normal radiation chemistry studies. An exhaustive search of the appropriate conditions for Cl_2 formation was not made, but a few systems did lead to measurable and reproducible Cl_2 production.

$CaCl_2$ was dried and then reloaded with known amounts of water and irradiated with γ-rays. The production Cl_2 was very dependent on the amount of water present. No Cl_2 was observed when water was absent. The *G*-value for Cl_2 rose to 0.035 molecule/(100 eV) at 1.5 wt % water loading and decreased to a value of 0.013 molecule/(100 eV) at 5.5 wt % water loading; see Figure 4. There appears to be optimum water loading for producing Cl_2. A small amount of water or OH groups is probably required to stabilize Cl_2 formation on the salt, but water decomposition products may dominate at higher water concentrations. Gaseous Cl_2 may be predominately formed with no water. The yield of H_2 with $CaCl_2{\cdot}2H_2O$ is relatively high, indicating that decomposition to H_2 may be preferred over that to Cl_2. Another possibility for the low production of Cl_2 is due to the preferential formation of HCl.

In the 5 MeV He ion radiolysis, no Cl_2 was observed in any $CaCl_2$ or $MgCl_2$ system. These systems included the same water loadings that gave observable Cl_2 production with γ-radiolysis. Either the Cl_2 yield with α-particles is very low or they have a very different water loading dependence than that observed with γ-radiolysis.[18,48] It is also possible that the 5 MeV He ion radiolysis leads to more production of gaseous Cl_2 than in γ-radiolysis or in more favorable conditions for the production of HCl. A thorough search may eventually discover the optimum conditions for observing Cl_2 formation, but the Cl_2 yields associated with the solid phase are certainly low for the salts examined here.

Conclusions

These experiments have examined the production of H_2 in the radiolysis of $CaCl_2{\cdot}2H_2O$, $CaCl_2{\cdot}6H_2O$, $Ca(OH)_2$, $MgCl_2{\cdot}2H_2O$, $MgCl_2{\cdot}6H_2O$, and $Mg(OH)_2$. Radiation chemical yields of H_2 do not show any particular trend with respect to the cation or the degree of hydration. The radiolysis of $MgCl_2{\cdot}2H_2O$ leads to the greatest yield for the formation of H_2, but the yields from both γ-radiolysis and helium ion radiolysis decrease with dose due to the radiolytic instability of the dihydrate. The H_2 yields with the other compounds are between 0.04 and 0.2 molecule/(100 eV), which is considerably lower than that from pure water or 2 M chloride solutions. However, these yields are considerably greater than that observed in the bulk radiolysis of CeO_2 and ZrO_2 with adsorbed water.

Molecular chlorine was determined in association with the solid salt and not in the gas phase. The production of Cl_2 is found only in the γ-radiolysis of $CaCl_2$ with a few weight percent of excess water loading. No Cl_2 was found in the 5 MeV He ion radiolysis of identical systems. None of the other compounds examined here showed detectable amounts of Cl_2 formation.

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