ATMOSPHERIC CHEMISTRY IMPACTS ON THE CORROSION ENVIRONMENTS OF WASTE PACKAGES

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Atmospheric chemistry affects the corrosion environment of high-level waste or spent nuclear fuel waste packages emplaced in a repository. The corrosion environment is chemically complex and dynamic. Additionally, gamma radiolysis due to decay of the waste inside the waste package affects not only liquid and solid materials on the waste package surface but also the air immediately surrounding the waste package. Because atmospheric dusts and aerosols may contain nitrates and organic materials, the local chemical environment on a waste package may have both reducing and oxidizing components; that these components can and do react has been demonstrated. Of particular interest is how the chemical environment can be defined so that appropriate corrosion tests can be conducted. The primary objective of this paper is to document what has been learned and provide a starting point for future corrosion environment determinations.

I. INTRODUCTION

In developing a prediction of the corrosion of waste packages or dry-storage canisters containing high-level waste or spent nuclear fuel, an initial question is: What is the corrosion environment? The Yucca Mountain Project addressed this question for waste packages emplaced in a repository and cooled by forced ventilation using outside, dust-containing air. The forced ventilation would last for 50 to 100 years or longer and cause some of the dust transported into the repository to accumulate on waste-package surfaces. Bryan[1] developed a prediction of the waste-package surface environment due to dust deposition using primarily the field work of Reheis and Kihl[2] on atmospheric dust compositions in the region of Yucca Mountain. Their objective was to answer questions about the relations of dust to local source lithology and geomorphic setting, distance from source, and climate. Bryan used the Reheis and Kihl information to develop a prediction of the soluble salt content of dust, which was in turn used to predict whether a corrosive environment would occur on a waste package surface. The corrosive-environment prediction model was largely based on nitrate and chloride ions in a deliquescent brine and the ratio of those ions in the brine. The model predicted that a high nitrate-to-chloride ratio would render the environment non-corrosive.

Additional information and analyses carried out after Bryan's work suggest that a different predictive model might be developed based on a more complete description of atmospheric dust composition and the chemical reactions that might occur in the dust itself and subsequently in deliquescent brines. A more detailed description of atmospheric dust composition and chemistry follows based on information found in the literature along with descriptions of reactions that might occur. The focus is on nitrate and chloride ions, organic species, and radiolysis, the reactions among them, and the resultant effects on the corrosion environment.

## II. ATMOSPHERIC DUST COMPOSITION AND CHEMICAL REACTIONS

Chemical reactions occur quite readily in the air among the components of dusts and the gas-phase. Chemical species in the atmosphere that originate from the surface of the earth are called "primary" components; an example of a primary component is calcium carbonate. Chemical species that are the result of chemical reaction in the atmosphere are called "secondary" components; an example is sodium nitrate.

The atmospheric dust compositions obtained from Reheis and Kihl focused primarily on the nitrate and chloride content. The dust collector used in their field work was an angel-food cake pan filled with glass marbles and mounted about two meters above the ground. As dust settled into this pan it would further fall into the marbles and not be blown away. Dust samples were retrieved at one- to two-year intervals from the collectors by washing the marbles with distilled water into plastic bottles. The sample was then gradually dried in the laboratory at about 35°C and coarse organic material removed.

Turpin and coworkers[3] report that 10 to 70% of the total fine dry particle mass in the atmosphere is composed of organic compounds. Jacobson[4] reports that organic material typically accounts for 5 to 50% of the total fine particle mass in dust and is often the largest component after sulfate and nitrate. Gelencér[5] provides in his book considerable detail on the organic composition of atmospheric dust. Thus it is realistic to conclude that
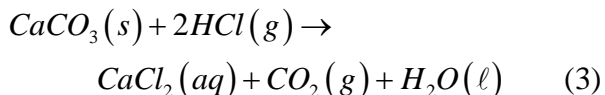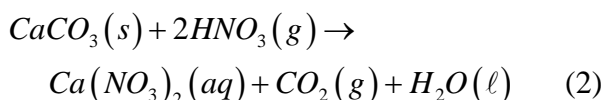
organic matter is a significant fraction of atmospheric dust.

Inorganic matter of interest includes not only nitrate and chloride, but also magnesium, calcium and other ions. Depending on the humidity level of the air, certain mixtures of magnesium, calcium, sodium, and potassium nitrates and chlorides can deliquesce at temperatures approaching 200°C.[1] It is well known that oxides of nitrogen such as nitric acid are produced photochemically in the atmosphere and by anthropogenic sources. These oxides of nitrogen undergo heterogeneous reaction with sea-salt sodium chloride to produce sodium nitrate and hydrogen chloride according to:[6]

$$NaCl(s, aq) + HNO_3(g) \rightarrow$$
$$NaNO_3(s, aq) + HCl(g) \qquad (1)$$
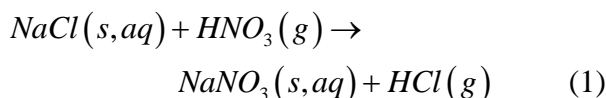
Where (s,aq) denotes solid (s) or aqueous (aq) and will depend on the relative humidity. Similar reactions with sodium chloride and other nitrogen oxides can also occur producing sodium nitrate along with the gas-phase components $ClNO_2$ and $ClNO$. Hydrochloric acid is also produced by anthropogenic sources, primarily combustion processes.

Calcium and magnesium carbonates are also commonly present in dust.[7] Given that the acid gases HNO_3 and HCl (along with H_2SO_4) are virtually always present in the atmosphere as noted above, the reaction of carbonates with these gases can be expected to proceed according to:[7]

$$CaCO_3(s) + 2HNO_3(g) \rightarrow$$
$$Ca(NO_3)_2(aq) + CO_2(g) + H_2O(\ell) \qquad (2)$$

$$CaCO_3(s) + 2HCl(g) \rightarrow$$
$$CaCl_2(aq) + CO_2(g) + H_2O(\ell) \qquad (3)$$

The products of these chemical reactions (1), (2), and (3) have been observed in the atmosphere. Laskin and coworkers[8] present for the first time field evidence that individual calcium carbonate particles can indeed be completely converted to calcium nitrate particles in the atmosphere. Furthermore, since long-term measurements of the region where calcium nitrate was observed show that calcium and magnesium carbonates together constitute more that 50% of the dust, one would expect that magnesium nitrate is also present in the dust. The transformation of calcite to calcium nitrate has been

observed in several parts of the world including the Middle East and China.[6]

Sullivan and coworkers[9] report that the major reaction product of chlorine-containing gases with dust is particulate-chloride and demonstrate that the uptake of chlorine by mineral dust particles in the marine boundary layer is due to heterogeneous reactions involving HCl(g). The uptake of chlorine by reaction of HCl(g) with calcite, which is present in virtually all dusts, has been demonstrated in the laboratory and occurs in an adsorbed layer of water.[10] The conclusion drawn by Sullivan and coworkers[9] is that they have shown that the reaction of HCl(g) with mineral dust is an important process in the atmosphere and involves complicated competitive exclusionary interactions with other reactants such as HNO_3 and SO_2.

Calcium chloride can also occur very rarely as a primary dust component. For example, calcium chloride is actively mined at the earth's surface in Bristol Dry Lake, California.[11] The temperature-humidity conditions at Bristol Dry Lake are sometimes such that the crystalline solid calcium chloride hexahydrate has been observed. Thus $CaCl_2$ can be lofted into the wind either as a deliquescent brine or as a solid.

Another reaction of interest is that of nitrate and organics. Nitrate and organics can react because one is an oxidizer and the other is a reductant, but at what temperature would it be reasonable to expect the reaction to proceed? Marshall and Peterman[12] report the composition of dust collected from the upper surfaces of steel canister heaters in Yucca Mountain which had been at ~200°C for two years and compare this composition with dust that was not heated. These compositions indicate that the heated dust was strongly depleted in nitrate relative to the unheated dust. Oliver[13] reports the results of experimentally heating atmospheric dust collected in the vicinity of Yucca Mountain, Nevada. Heating atmospheric dust samples to 160 to 180°C for two months resulted in a significant loss of nitrate but very little change in chloride. The nitrate-to-chloride ratio dropped by approximately two orders of magnitude. Oliver reports that the "lower NO_3/Cl in the heated dust samples likely is due to reduction of NO_3 by the oxidation of organic materials." The heating experiments were conducted in relatively dry air, not in the elevated-humidity environment expected in a repository at Yucca Mountain soon after closure. The experiments do reflect, however, what might be expected on the outside of a dry-storage canister containing spent nuclear fuel.

III. RADIOLYLSIS

Gamma radiation will be present at the outside surfaces of loaded waste packages and dry-storage canisters. Radiolysis will produce oxides of nitrogen and nitric acid in moist air.[14] Gaseous nitric acid can be adsorbed onto the waste-package or dry-canister surfaces and become a component of the dust. Observations from the spent fuel test at Climax revealed that carbon-steel liners of boreholes that had housed canisters containing spent fuel showed much more corrosion near the top than liners in boreholes that contained electric simulators.[15] The additional corrosion may have resulted from the production of nitric acid and other oxidizing chemical species by the irradiation of moist air. Reed and Van Konynenberg also describe the effect of ionizing radiation on moist air systems.[16]

Gamma radiolysis studies on sodium chloride, which can certainly appear on the outside of a spent nuclear fuel waste package or dry-storage canister, have resulted in a well-known damage effect in the alkali halides where the principle damage consists of bubbles of fluid halogen.[17] No other studies are currently known where an atmospheric dust containing a chloride salt has been exposed to radiation fields expected to occur on the surface of waste packages and dry-storage canisters.

IV. PHYSICAL CHEMISTRY AND REACTIONS IN SALT SYSTEMS

The loss of nitrate in atmospheric dust due to reaction with organic material in atmospheric dust would appear to result in a decrease in the nitrate-to-chloride ratio if chloride is not consumed. However, according to Bryan chloride may volatilize out of an aqueous solution containing chloride ion by "acid-gas devolatilization,"[1] as the following reaction sequence indicates:

$$H^+ + Cl^- \Leftrightarrow HCl(aq) \Leftrightarrow HCl(g) \qquad (4)$$
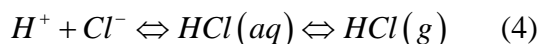
The water required for this reaction can come from either a brine or sorbed water on the dust. But, as in the case above showing the reaction of the atmospheric gases HNO_3 and HCl with calcite, is there experimental evidence indicating that acid-gas devolatilization occurs? According to Brendler and Voigt[18] small amounts of HCl gas can be released during the conduct of isopiestic experiments conducted at temperatures greater than 155°C using $MgCl_2$ for a reference solution, and because of this acid-gas release a $CaCl_2$ reference solution is preferred because it is more stable. Isopiestic experiments measure the vapor pressure of water vapor in equilibrium with salt solutions and are conducted in a closed system containing several solid salts in separate

sample cells with a little water (liquid) in a separate cell. The uptake of water by the salts is monitored, and the salts eventually form salt solutions. All samples have the same total pressure and water vapor pressure at equilibrium. A reference salt whose solution vapor pressure is (well) known yields the vapor pressure in equilibrium with all the other samples which are then analyzed for salt concentration. No further explanation was given by Brendler and Voigt[18] on why or how a solution of $MgCl_2$ releases HCl gas in an isopiestic experiment, and there currently appears to be no definitive experiment demonstrating on a material-balance basis that this phenomenon occurs for solutions of $CaCl_2$ at temperatures of interest. The binary system $MgCl_2 - H_2O$ has been studied at temperatures ranging from 130 to 250°C (Ref. 19) with no report of HCl(g) production in an autoclave experimental system.

Some insight on HCl(g) release from chloride salts can be obtained by examining thermogravimetric experiments conducted on calcium chloride and magnesium chloride hydrates.[20] The thermogravimetric results for magnesium chloride hexahydrate in an open vessel indicate that one mole of HCl evolves at 190°C per mole of $MgCl_2$ and the second mole of HCl evolves at 250°C; in a closed system these HCl-evolution temperatures are higher by about 50°C. The same experiment also investigated the $CaCl_2$ hydrates with no observation of the evolution of HCl up to 200°C. All these experiments were conducted one atmosphere total pressure. These thermogravimetric experimental results indicate that thermal decomposition of the salt hydrate occurs. Thus, thermal decomposition of a crystalline solid such as $MgCl_2$ hydrate producing HCl(g) could occur at one atmosphere total pressure on a waste package if the temperatures become high enough to mimic the thermogravimetric conditions.

The thermodynamic properties of the $CaCl_2 - H_2O$ system have been extensively investigated for the purpose of using this system as a reference for conduct of isopiestic experiments between 100°C and 250°C .[21] The results of this investigation can be used to predict the dry-out temperatures of the $CaCl_2 - H_2O$ system at various total pressures; at one atmosphere total pressure the dry-out temperature is very close to 160°C. There is no report of the evolution of HCl at that temperature. The temperature range investigated in the these experiments appears to be in the range of temperatures expected for waste packages immediately after closure in a repository similar to the design of the Yucca Mountain repository.[22]

Thus far acid-gas devolatilization has been considered only for the aqueous-chloride-salt system. Upon the addition of carbon dioxide to the system

evolution of HCl can occur under certain ambient-atmospheric conditions according to:[7]

$$CaCl_2(ai) + CO_2(g) + H_2O(\ell) \rightarrow$$
$$CaCO_3(s) + 2HCl(g) \qquad (5)$$
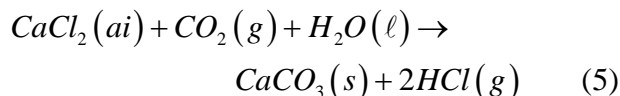
Where (ai) denotes the aqueous-ionized salt in solution. The extent of this reaction at temperatures, relative humidities, and CO_2 concentrations expected on a waste-package surface has not been investigated.

V. CONCLUSIONS AND OBSERVATIONS

The description of the corrosion environment on a waste package has evolved considerably. The potential for existence of calcium chloride and calcium nitrate in atmospheric dust has been confirmed. These components can be important because they can result in deliquescent solutions with dry-out temperatures approaching 200°C.[1] Along with inorganic components atmospheric dust contains a significant fraction of organic material, which can and does react with nitrate at the temperatures expected to occur on the surfaces of waste packages. Whether or not the reaction would occur at temperatures expected on the metal surfaces of dry-storage canisters is not known.

The dust deposited on these metal surfaces will result in a reacting system with a continual supply of components as long as air flows across the waste packages and dry-storage canisters. Even if the fresh air supply were terminated, gamma radiolysis will result in a continual supply of oxides of nitrogen and nitric acid to the metal surface. It is not known if the metal surfaces will ultimately become nitrate rich. This then implies that the corrosion investigation should be conducted in the presence of gamma radiation or some appropriate surrogate.

One topic that has not been discussed here is that of a material balance for all these components. What will be the mass of dust and reaction products on the metal surfaces as a function of time? From the corrosion side of the investigation is there a threshold concentration of any particular chemical species below which corrosion, such as chloride-induced stress corrosion cracking, does not occur? For the case of dust particulate this last question might be meaningless because the concentration will appear to be quite high where the particle "touches" the metal.

Can a meaningful long-term corrosion experiment be designed with a static corrosion environment? Probably not. It appears that some type of a dynamic system must be designed to duplicate what would occur in a repository or dry-storage system. Alternatively, some sort of static bounding corrosion environment might be devised. But this bounding corrosion environment might need to be very aggressive to ensure that it is indeed bounding. In any case, because of the radiolysis component of any spent nuclear fuel waste package or dry-storage canister, consideration must be given to the conduct of corrosion experiments with a gamma-radiation component or suitable surrogate.

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