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ABSTRACT

The extent of reaction of alloy-22 with limited amounts of aqueous calcium chloride (CaCl_2) was investigated. Alloy-22 is a highly corrosion-resistant nickel-chromium-molybdenum-tungsten alloy. Specimens were polished to a mirror finish prior to aerosol salt deposition. An aqueous film was formed by deliquescence of deposited CaCl_2 at 150°C and 22.5% relative humidity (RH). The reactant gas was a continuous flow of purified humidified laboratory air. The reaction progress as a function of time was continuously measured in-situ by a micro-balance. An initial weight gain due to deliquescence of the CaCl_2 was observed. A steady weight loss was observed over the next 72 hours, after which no further weight change was observed. During this weight loss, white precipitates formed and the specimen's surface became visibly dry. The precipitate crystals were identified as $\text{Ca}(\text{OH})_2$ by post-test Raman spectroscopy; however, energy dispersive X-ray spectroscopy indicated that there was a significant amount of chlorine contained in them.

INTRODUCTION

Alloy-22 is a highly corrosion-resistant nickel-chromium-molybdenum-tungsten alloy. The resistance to corrosion of alloy-22 in various aggressive environments has made it a primary candidate for use in the outer layer of nuclear waste containers within the Yucca Mountain nuclear waste repository. Radiative decay of contained nuclear waste is predicted to produce a range of temperature and relative humidity (RH) conditions within the repository over its operating period. Even in the most extreme predicted environments (ca. 160°C and 18%RH), deliquescent salts such as CaCl_2 are capable of forming concentrated aqueous solutions; thus, thin film aqueous corrosion will be a likely mode of container degradation in the Yucca Mountain repository.

Thin aqueous film corrosion processes produce changes in the aqueous film chemistry that significantly affect the extent of the corrosion reactions. At cathodic sites oxygen reduction to hydroxyl ions causes elevation of pH, and at anodic sites dissolved metal hydrolysis causes decrease of pH. Electrolyte migration further occurs to maintain electrical neutrality. These changes in solution chemistry can result in precipitation reactions and acid gas generation. These electrochemical processes have been observed to ultimately limit the extent of corrosion for a given amount of aqueous salt film.

EXPERIMENTAL

Alloy-22 specimens with nominal dimensions 51mm x 13mm x 1.5mm were polished to a mirror finish, with a final polish of 1 μ m Al₂O₃. A dilute calcium chloride solution was prepared by dissolving 5g CaCl₂-dihydrate (reagent grade, Mallinckrodt) in 500mL de-ionized water. The calcium chloride solution was sprayed into the coating chamber as an aerosol for uniform specimen coating. Specimens were coated with a thin CaCl₂ film as follows. Specimens were first heated for 10s in the stream of a hot air gun; specimen preheating and subsequent heating/drying between coating steps is necessary in order to achieve a uniform coating. Heated specimens were then introduced into the nebulizer chamber for 2s, then removed and dried in the hot air stream; this process was repeated until the desired coating was achieved. Specimens were weighed before salt deposition, and periodically during the coating process to determine how much salt had been deposited. A final mass of 3mg \pm 0.2mg of CaCl₂ was ultimately deposited on the surface of each specimen.

A Cahn TG-100 thermogravimetric analyzer was modified such that the sample chamber would be capable of achieving stable maximum environmental conditions of 22.5%RH at 150C. The reactant gas was a continuous flow of purified humidified laboratory air; microbalance purge gas was ultra high purity He. Humidity was achieved and controlled by varying the ratios of dry air and air being bubbled through a vapor generator. Temperature and RH were measured continuously using sensors that were situated within the sample chamber approximately 1cm below the bottom of the hanging specimen. Specimen mass was recorded as a function of time, as measured in situ via the TGA microbalance, which is sensitive to changes of \pm 1 μ g with an average noise resolution of \pm 5 μ g.

Immediately following the coating process, specimens were introduced into the TGA sample chamber and allowed to equilibrate at the desired temperature and a very low relative humidity (nominally 2%RH). After the equilibration period (10-15min) the balance was tared and the relative humidity in the sample chamber was increased to the desired setpoint. An increase in specimen weight was observed as the RH passed through the deliquescence point of CaCl₂. After \sim 30min in a constant temperature and RH environment, the initial salt coating was observed to have formed an equilibrium thin aqueous film on the surface of the specimen, which was visibly wet. Subsequent reaction progress was monitored as a function of specimen weight change. Insoluble crystalline precipitates were observed to form on the specimen surface, which in turn became gradually drier as the nondeliquescent crystals allowed for water to evaporate from the surface. This process was observed gravimetrically as a steady weight loss. After sufficient time, the specimen surface appeared completely dry and covered uniformly with crystalline precipitates.

Various methods of analysis were performed on post-test specimens in an attempt to characterize the reaction products. Raman spectra of precipitate crystals were achieved using a XXXXXXXX Spectrometer. Scanning electron microscopy and X-ray elemental mapping were performed using a XXXXXXXX electron microprobe (EPMA).

DISCUSSION

The reaction of CaCl_2 on the surface of Alloy-22 at 150°C and $22.5\% \text{RH}$ is displayed gravimetrically as a function of time in Figure 1. The initial weight gain is attributed to water absorption due to the deliquescence of CaCl_2 . Subsequent weight loss is accompanied by insoluble precipitate formation, water evaporation, and acid gas evolution. Gravimetric equilibrium is reached in ~ 24 hrs, and no further weight change is observed.

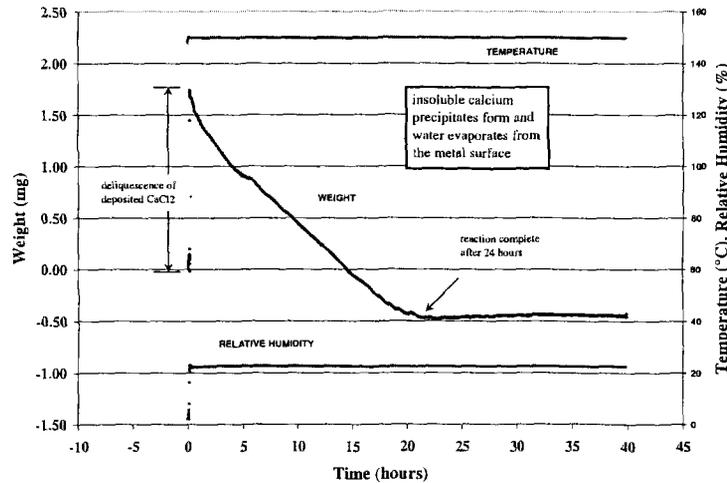


Figure 1. Weight change and T, RH curves for a typical test at 150°C and $22.5\% \text{RH}$.

Temperature effects on the reaction rate of CaCl_2 on the surface of Alloy-22 at a constant relative humidity of 22.5% are illustrated in Figure 2. At 100°C there was no observable change in weight following the initial increase due to deliquescence. At 125°C a very

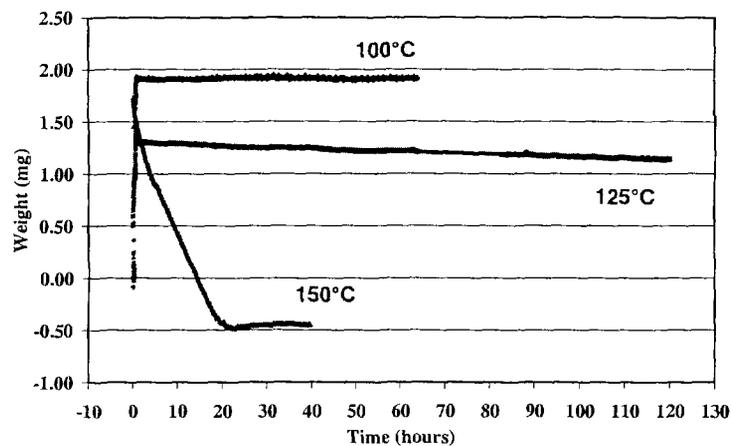


Figure 2. Comparison of gravimetric changes of CaCl_2 -coated alloy 22 specimens at 100°C , 125°C , and 150°C .

subtle yet steady weight loss was observed for more than 600hrs. At 150C a sharp decline in weight was observed following initial deliquescence, and reaction completion was reached in ~24hrs.

Post-test electron probe microanalysis and x-ray elemental mapping were performed on the Alloy-22 sample that had been in the 150C 22.5%RH environment. Figure 3 shows the elemental distribution of chloride, calcium, and oxygen relative to a secondary electron image. The chloride, calcium, and oxygen distributions show a uniform precipitate composition with respect to these three elements. No other elements were detected within the precipitate species.

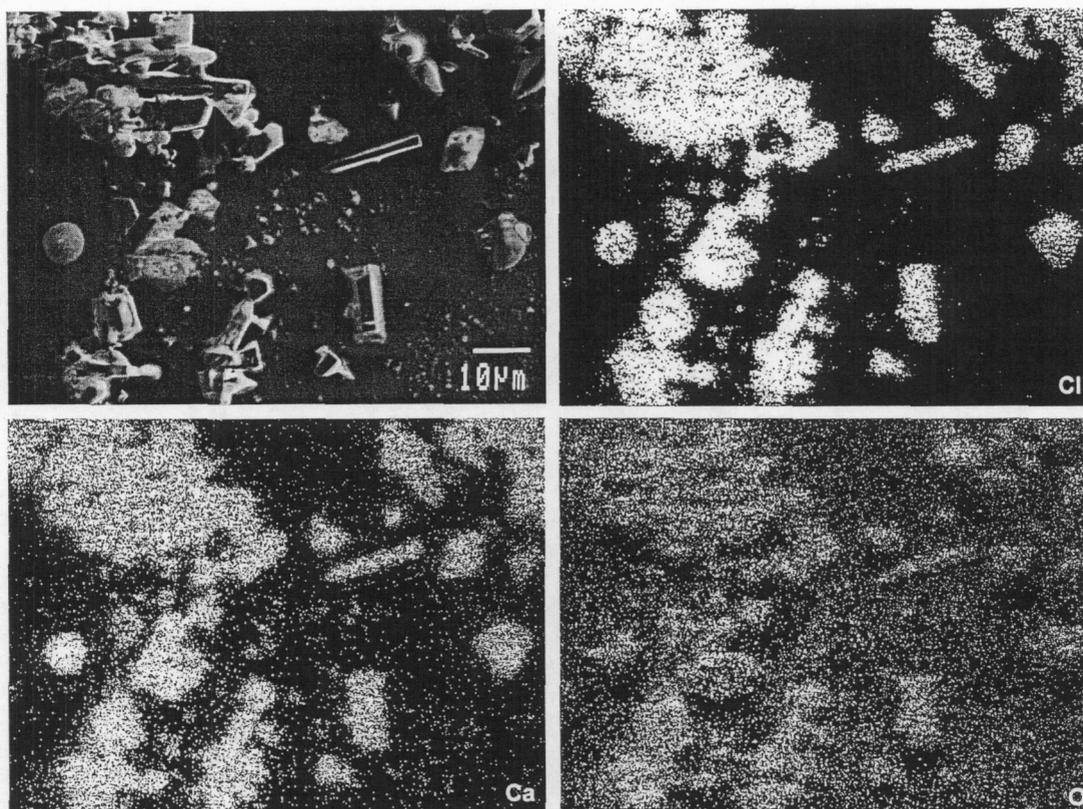


Figure 3. SEM image (top left) of crystalline precipitates on the surface of alloy 22, and X-ray distribution mappings by EPMA of Cl, Ca, and O. (intensity is not normalized)

Lack of metal ion incorporation in the precipitates suggests that the primary reaction responsible for the gravimetric changes may not be an electrochemical one, and indeed may be independent of the substrate. Various substrates were thus tested in conditions identical to the alloy-22 experiment at 150C and 22.5%RH in order to probe the nature of the CaCl_2 – substrate interaction. In addition to alloy-22, substrate specimens of platinum, glass, and alloy-825 were tested. The gravimetric reaction progress for calcium chloride films on the surface of these four different substrates is summarized in Figure 4. While slight variances in reaction rate (gravimetric slope) were observed, the reaction progress on all four substrates achieved completion in ~24hrs. Variances in weight loss slopes and final overall mass losses are likely due to minor differences in coating uniformity.

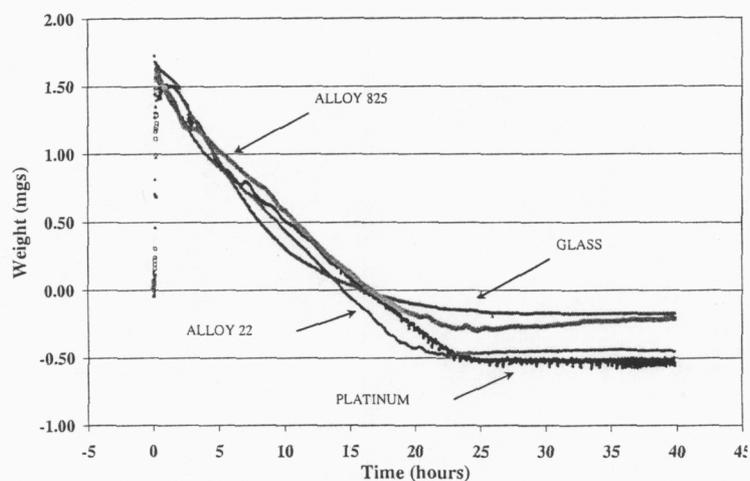


Figure 4. Gravimetric comparison of four CaCl₂ coated substrates at 150C and 22.5%RH.

Raman spectroscopy confirmed that the crystalline precipitates were identical on the alloy-22, glass, and platinum substrates. The alloy-825 specimen yielded regions of localized electrochemical attack made evident by reddish-brown ferrous oxide precipitates (Figure 5). This can be expected, as alloy-825 contains a significant amount of iron and is thus less corrosion-resistant than the nickel-laden alloy-22.

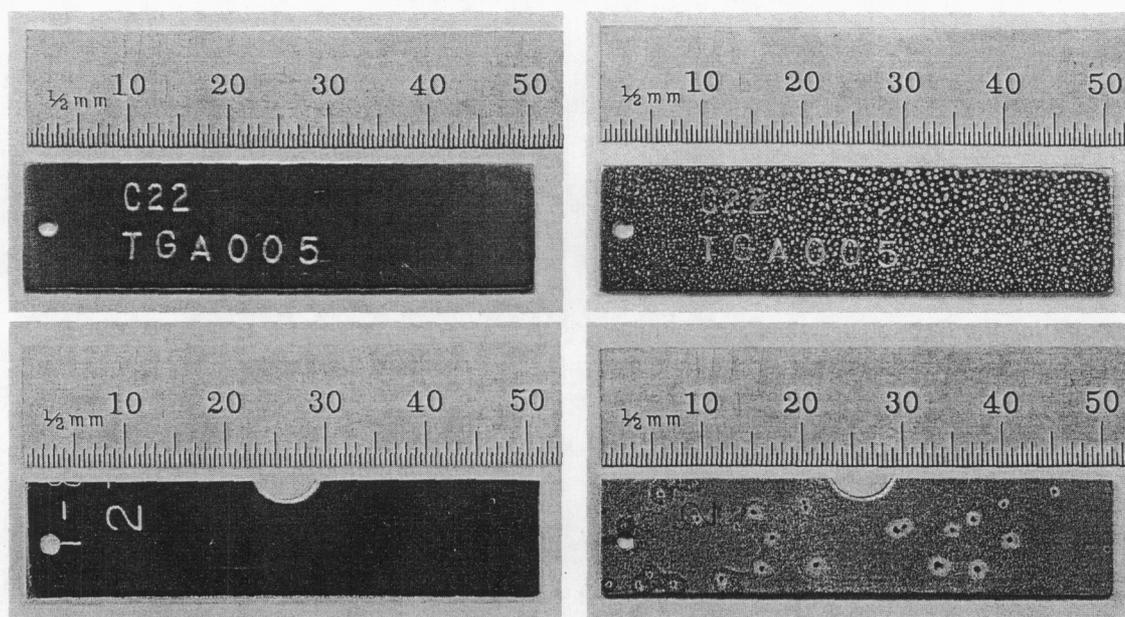


Figure 5. Optical comparison of alloy 22 (top) and alloy 825 (bottom) specimens before coating (left) and after reaction with CaCl₂ (right) at 150C and 22.5%RH.

CONCLUSIONS

At high temperatures, thin aqueous calcium chloride films undergo precipitation reactions that ultimately serve to limit the extent of reaction with the substrates with which they are in contact. Aqueous films that are formed through deliquescence are by nature extremely

concentrated (deliquescent calcium chloride films formed at 150C and 22.5%RH were calculated to be ~16*m*). Furthermore, concentrated calcium chloride solutions are known to be acidic. Thus, in an open system at ~1atm and 150C the partial pressure of hydrochloric acid is not sufficient to keep it in solution, and HCl gas volatilization results; the solution pH is thus raised, causing precipitate formation. As the soluble calcium chloride is converted to insoluble Ca(OH)Cl, water is free to evaporate from the aqueous layer in a self-limiting process. This simple chemical reaction accounts for the majority of gravimetric change seen on all four coated substrates at high temperatures. In the case of alloy-825, a secondary electrochemical process was observed, leading to precipitation of insoluble ferrous oxides.

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