Corrosion of Polymer–Concrete Composites in Hydrochloric Acid at Elevated Temperature*

R. S. YEO,** *Electrochemical Technology Group, Brookhaven National Laboratory, Upton, New York 11973*, A. N. ZELDIN and L. E. KUKACKA, *Process Sciences Division, Department of Energy and Environment, Brookhaven National Laboratory, Upton, New York 11973*

Synopsis

A series of polymer–concrete (PC) materials were evaluated in 30% hydrochloric acid at 90°C. It was shown that a polymer aggregated with quartz sand is a potential candidate for use in coating or construction materials for hydrogen–chlorine energy storage systems. The results have shown that the corrosion rate of PC in this solution is a diffusion-controlled process. The major weight loss can be attributed to the presence of cement in the PC samples. The influence of the sand/cement ratio, and the crosslinking agent content on the corrosion of PC samples is also discussed.

INTRODUCTION

In many energy conversion and storage processes, material problems may be severe because of extremely corrosive environments, as for example in geothermal wells,[1] chloroalkali cells,[2] and hydrogen–halogen energy storage systems.[3–5] HCl injection into geothermal brine as a method of reducing scale formation has been proposed.[6]

A hydrogen–chlorine energy storage system operates at about 90°C.[3] The fluid circulated throughout the system is predominately HCl along with chlorine, which is both highly corrosive and oxidizing. In addition, an essential requirement for an energy conversion or storage system is that it must be cost effective, and therefore low-cost construction or coating materials are required.

There are not many materials suitable for use in high-pressure operation with hot HCl containing dissolved chlorine. Glass, ceramic, and poly(tetrafluoroethylene) exhibit excellent resistance to corrosion, but suffer from the high-pressure limitation. Tantalum meets all the requirements of corrosion resistance and high-pressure utilization, but is expensive.

Polymer concretes (PC) have been considered as containment materials. They are composites with strength and durability characteristics far superior to those of Portland Cement concrete, and they are being utilized in applications where Portland Cement cannot be used or where there are severe maintenance problems.[7] The material combines the usefulness of both organic binders and inorganic filler components and has improved chemical resistance. The feasibility of using PC composites as construction materials for handling hot brine was demonstrated in 1972.[8] It was observed that the composites had long-term

stability in seawater at 177°C and in dilute acid solutions. Also, the results indicated that the PC material has good durability in hot brine solutions and steam, at temperatures up to 250°C.[9]

Furthermore, it was also shown that PC composites have durability and chemical resistance to 0.36% (0.1N) HCl solutions.[10] In that investigation, composites consisting of 55 wt % styrene (St)–36 wt % acrylonitrile (ACN)–9 wt % trimethylolpropane trimethacrylate (TMPTMA), in conjunction with a sand–cement filler in a ratio of 9:1, were exposed to 0.36% HCl for 1000 days at 90°C. After the exposure, the coefficient of water absorption of the samples increased from the range of 1.5–2.0% to the range of 4–4.5%, and the compressive strengths decreased by 10–15% of the initial values.

In light of these results, it was therefore of interest to explore the feasibility of using PC composites as construction or coating materials for handling the Cl_2/HCl corrosive solutions. In this study, a variety of PC samples were prepared and tested in 30% HCl at 90°C. Finally, the sample which showed stability in hot concentrated HCl was also examined in the hot HCl/Cl_2 environment.

EXPERIMENTAL

Materials and Sample Preparation

Polymer-concrete samples consisting of organic binders and inorganic fillers were used in this study. The vinyl-type monomers used, St, ACN, Aa (acrylamide, and TMPTMA, were all commercially available and did not require further purification. A silane coupling agent (A-174) with methacrylate functional groups was used to obtain a stronger chemical binding of the organic and inorganic phases. Sand and type III Portland cement were used as an aggregate composition for producing high-quality PC with a minimum polymer content. The sand utilized was a mixture of different particle sizes (sieve opening 1180, 600, and 150 μm, in the ratio 50:25:25, respectively). Type-III Portland cement was supplied by the Universal Atlas Co. and the chemical composition was 19.1% SiO_2, 7.1% Al_2O_3, 61.8% CaO, 2.8% MgO, and 3.7% SO_3. The method of preparing PC material has been described in detail previously.[11]

Analytical reagent grade HCl (37%) obtained from the Mallinckrodt Co. and doubly distilled water were used in preparing the test solution. Chlorine (99.5%) was used without further purification.

Test Methods

The compositions and dimensions of the PC samples tested in this study are listed in Table I. The samples were either of cylindrical shape or a flat piece. Each sample was dried overnight in vacuum at 70°C. The initial weight of the sample was determined prior to its introduction into the solution. After a certain time period, the sample was removed from the solution, dried in vacuum at 70°C, and its weight determined. The same procedure was then repeated, the sample was replaced in the solution for additional time periods, and the weight changes were determined. The corrosion tests were all performed at 90°C. Unless otherwise specified, the test solution is 30% HCl.

TABLE I
Compositions and Dimensions of PC Samples[a]

Sample No.	Aggregate, 88 wt %		Polymer, 12 wt %				Sample dimensions, cm
	Sand, %	Cement, %	St, %	ACN, %	Aa, %	TMPTMA, %	
1	90	10	55	36		9	4.3 × 2.4 × 0.40
2	90	10	50	33		17	6.2 × 2.5 × 0.30
3	90	10	50	20		30	3.0 diam × 2.16
4	80	20	55	35	5	5	3.0 × 2.3 × 0.35
5	70	30	55	35	5	5	3.1 × 2.8 × 0.55
6	60	40	55	35	5	5	3.7 × 3.0 × 0.55
7	50	50	55	35	5	5	3.0 diam × 1.30
8		100	50	33		17	3.0 diam × 1.04
9	90 glass	10	50	33		17	3.0 diam × 1.00
10	90 quartz sand	10	50	33		17	3.0 diam × 1.05
11	100 quartz sand	0	50	33		17	3.0 diam × 1.00

[a] St = styrene; ACN = acrylonitrile; Aa = acrylamide; TMPTMA = trimethylolpropane trimethacrylate.

RESULTS AND DISCUSSION

The rate of corrosion may be determined either by interfacial reactions or by diffusion processes. In interfacial processes, the corrosion is controlled by diffusion either in the corrosion products or across a degraded region, and the rates decrease with time. The rate of penetration, dx/dt, is then given as

$$dx/dt = DA(\Delta c/x) \tag{1}$$

where D is the diffusion coefficient of the dissolved species, Δc is the concentration gradient between the dissolving interface and the surface of material, A is the effective area across which diffusion takes place, and x is the diffusion length which is often equal to the corrosion depth.

Equation (1) can be integrated to give

$$x = Kt^{1/2} \tag{2}$$

where K is a constant related to the diffusion coefficient and the value of x can be determined from the weight loss data.

Figure 1 presents the results of PC weight changes for various sand/cement ratios with the same polymer composition of 55% St–35% ACN–5% Aa–5% TMPTMA (samples 4–7 in Table I). The results for niobium are also included for comparison. The unity slope of the log–log plot shows that niobium corrodes at a constant rate indicating a surface-controlled reaction. On the other hand, the corrosion for PC is initially high. The slope on the log–log plot is 0.4, suggesting that the corrosion is diffusion controlled. The corrosion rate of PC decreases with increasing sand/cement ratio for the same monomer composition. Also, weight loss drastically increases for samples consisting of less than 65% sand in the aggregate.

Cement consists of oxides which are soluble in acid, whereas sand is essentially silicate which is inert to acid. The samples were initially grey and became cream colored after exposure to the acid, suggesting that the cement component had dissolved. It was shown previously[12] that the properties of PC are strongly related to the sand/cement ratio. The strongest and generally most durable PC
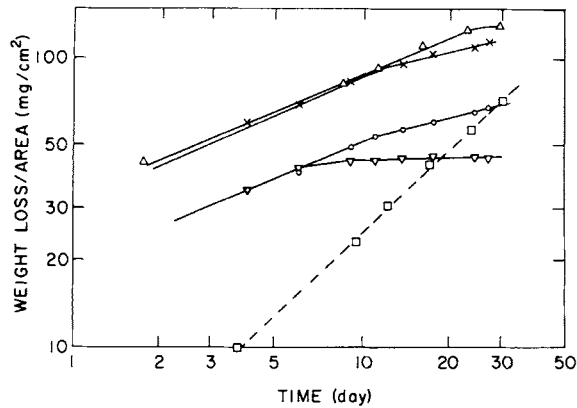
Fig. 1. Weight loss per unit area vs. time for PC samples with various sand/cement ratios. ∇, sample 4; O, sample 5; x, sample 6; Δ, sample 7; $\square$, niobium.

is produced when 65–90 parts of sand are used with 35–10 parts of cement. The polymer molecules, which are absorbed by the particles of the filler, produce an oriented microlayer. The energy of the adsorption bond depends on the surface energy. The carrier of high surface energy during the formation of PC is sand.[12] The uniformity of contact between sand and polymer decreases as the amount of sand is less than 65%, and thus destroys the mechanical strength and chemical stability of the PC composite.

The results also indicate that the corrosion rate is likely to be related to the size of the samples, thinner samples corroding more rapidly than thicker samples; but, as the corrosion rates were too high for practical application, this possibility was not pursued.

Another fact that appears to be related to sample size is the decreasing corrosion rate of sample 4, which was almost zero after a week, while the corrosion for other samples persisted. This difference is clearly related to the thickness of the sample. Sample 4 was the thinnest (0.35 cm thick), and the corrosion process precipitated through the whole sample after a week. Corrosion was also evident in the cream color visible through the cross section of a fractured sample, whereas the center portions of the other three samples remained varying shades of grey. In addition, as shown in Table II, the total weight loss for sample 4 is

TABLE II
Summary of Results of Polymer Concrete Weight Loss

Sample No.	Initial cement content, wt %	Weight loss after 25 days, wt %
1	8.5	5.7
2	8.5	5.7
3	8.5	2.8
4	17.0	16.3
5	25.5	15.0
6	34.0	21.3
7	42.5	15.5
8	85.0	35.5
9	8.5	5.1
10	8.5	2.7
11	0.0	0.2

essentially equal to the initial content of cement in the sample. For the other samples, the total weight loss after 25 days is less than the initial amount of cement in the sample. These results are mentioned to indicate that only the earlier parts of the curves in Figure 1 relate to the rates of corrosion or leaching in the samples, whereas the later parts are affected by size limitations of the samples.

The influence of the ACN and TMPTMA content on the corrosion of PC was also studied and the results are shown in Figure 2. It is clear that for the sample containing lesser TMPTMA, the corrosion is smaller. PC composites have high durability and thermostability when a three-dimensional polymer structure is formed. Therefore, the presence of a crosslinking agent such as TMPTMA or divinyl benzene is essential. The amount required will be dependent upon the service environment.

The concentration of the crosslinking agent affects not only the properties of PC but also the required ACN concentration. It is seen in Table I that the ACN/St ratio increases with decreasing TMPTMA concentration. As has been shown previously,[13] if the initial concentration of ACN is less than 27 mole %, polystyrene is formed along with the copolymer. The homopolymer does not mix with the copolymer, and thus yields a heterogeneous product which is thermochemically weak. As a result, the penetration of solution is large and the durability of the PC composite to thermoxidation and corrosion is small.

Figure 3 shows the results for one polymer with various aggregates (samples 8–11) and fixed sample size and shape. The polymer composition is 50% St, 33% ACN, and 17% TMPTMA. The polymer aggregated with quartz sand is over an order of magnitude more resistant to corrosion on this environment than the PC samples which contain the acid-soluble components. This is again consistent with the above observations that the corrosion rate is a diffusion-controlled process and cement is the component leading to the major weight loss.

Handling of dry chlorine gas presents no particular problems from the standpoint of corrosion as it is inert to many metals, such as titanium, but it is
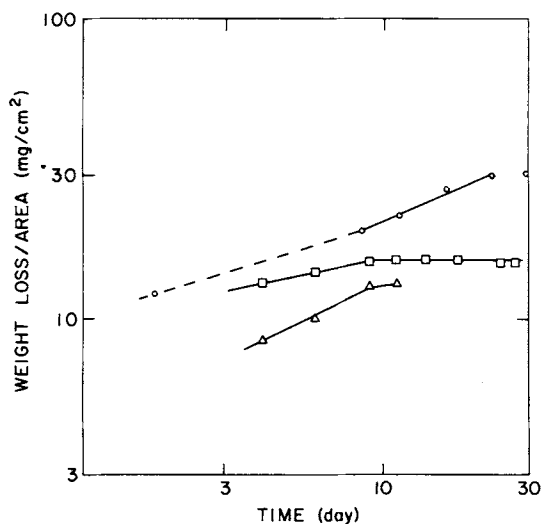

Fig. 2. Weight loss per unit area vs. time for PC samples with different TMPTMA concentrations. △, sample 1; □, sample 2; ○, sample 3.
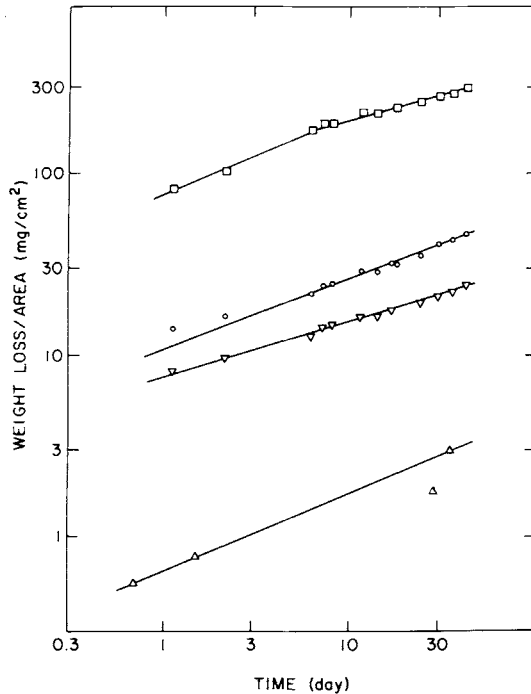
Fig. 3. Weight loss per unit area vs. time for different sand/cement ratios. □, sample 8; O, sample 9; ▽, sample 10; △, sample 11.

highly corrosive if heated or if some moisture present results in the formation of small amounts of dilute HCl. It is of interest to evaluate the corrosion of polymer–quartz sand in the hot HCl/Cl_2 environment. The sample was tested up to 80 days, and the results are shown in Figure 4. The data for a polymer sample without quartz sand are also shown in the same figure. The weight of the sample increases with time, suggesting that there is very little corrosion in HCl/Cl_2. The large weight increases of the polymer may be due to the fact that the polymer can be hydrolyzed or chlorinated. The increase of the weight of the polymer–quartz sand composite is likely due to the weight increase of the polymer component in the composite as a result of absorption.
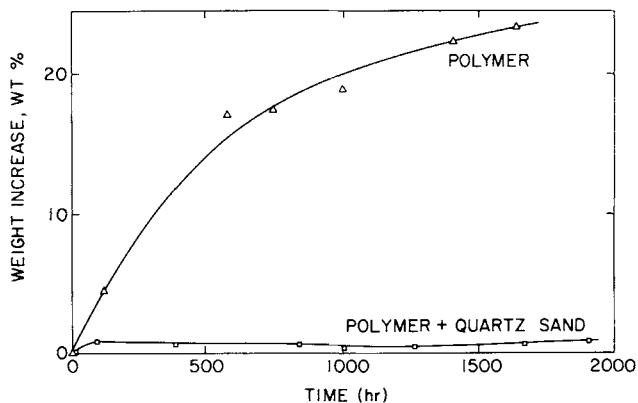

Fig. 4. Weight change vs. time for PC and polymer samples. HCl/Cl_2 environment at 90°C.

SUMMARY

The results of this study indicate that composites consisting of polymer–quartz sand are corrosion resistant to 30% HCl or HCl/Cl_2 environments at temperatures up to 90°C; and it is feasible to consider their use in hydrogen–halogen energy storage systems. The results also indicate the importance of the proper aggregate selection and composition in the formation of durable PC composites for use in highly reactive environments.

The use of cement as a reactive filler in PC results in weight losses when the samples are exposed to hot 30% HCl solutions. Earlier work has indicated that the corrosion resistance of PC to hot brine and 0.36% HCl solution is enhanced by the addition of cement to the composite.[10] These differences are likely due to the increased HCl concentration, the geometric characteristics of the samples tested, and the length of the exposure time.

On the basis of the results from earlier and current studies, it appears that PC composites, containing silica–Portland Cement fillers, are suitable for use in geothermal environments where the hydrogen-ion activity is greater than 5. Additional tests should be performed to determine whether these composites can be used in lower pH environments and at what pH concentration the use of Portland cement is detrimental.

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