DEGRADATION OF MATERIALS UNDER CONDITIONS OF THERMOCHEMICAL CYCLES FOR HYDROGEN PRODUCTION – PART III

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Abstract

A capsule method was employed to screen a number of materials for degradation under selected conditions of the sulphur-iodine (SI) and the copper-chlorine (Cu-Cl) thermochemical cycles. A summary of the results of an experimental investigation is given. The recommendations for the selection of the materials required for the construction of the electrolyser subsystem of the copper chlorine hybrid cycle are presented and discussed with the associated rationale. Some remaining uncertainties are illustrated on the basis of the experimental evidence gathered.

1. Introduction

Selection of materials is one of the major challenges for implementation of thermochemical cycles for hydrogen production for the future hydrogen economy. In this paper, we present a summary of the results of an experimental investigation to screen selected materials for degradation under selected conditions of the sulphur-iodine (SI) and copper-chlorine (Cu-Cl) thermochemical cycles. Partial results, with many pertinent details, were presented previously ([1], [2]). This paper attempts to summarize the conclusions reached to date.

A hydrogen thermochemical cycle is an industrial process in which the overall net reaction is that of the decomposition of water into hydrogen and oxygen. The net input into the process is energy (heat, or heat and electricity) and water, while the output consists solely of pure hydrogen and oxygen gases (see Figure 1). Any other chemicals used internally in the process are fully recycled. Many candidate thermochemical cycles have been suggested as potential pathways to the future "hydrogen economy", the SI and Cu-Cl cycles being among the most prominent ones.

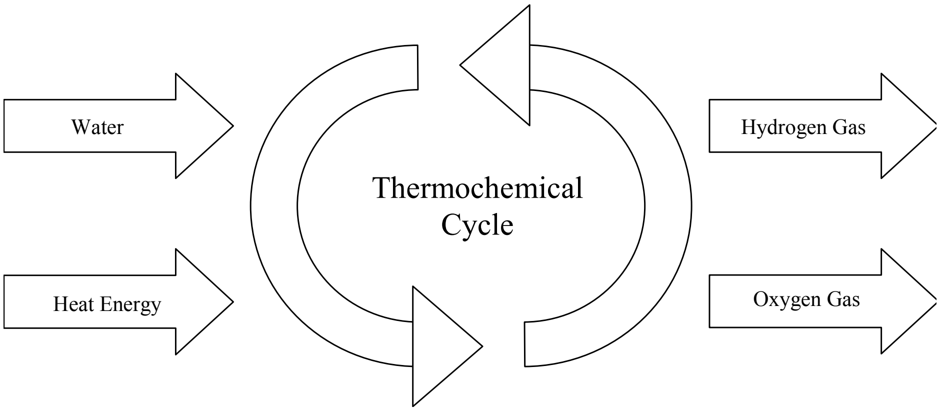

Figure 1 Diagram illustrating water decomposition in a thermochemical cycle.

Hydrogen economy is a vision for the use of hydrogen as the prevailing fuel in common transportation and industrial applications that require a portable fuel source with high energy density, and possibly also in many stationary applications. Widespread use of hydrogen would greatly reduce the current reliance on fossil fuels and thus reduce greenhouse-gas emissions, without adverse technological side effects. Hydrogen as an energy source is exceptionally clean because oxidation of hydrogen (either by combustion or in fuel cells) produces only water at the point of energy use. The usage of non-fossil-derived power would produce no greenhouse gas emission at the point of hydrogen production. In contradistinction to the economies based on petroleum and coal, fuel for the hydrogen economy would be sustainable indefinitely. A future CANDU®[1] power plant could serve as the source of energy (heat, or heat and electricity) for the production of hydrogen to drive the hydrogen economy. The co-generation of hydrogen and electricity appears to be a good match because of the combination of the nuclear power plant technical and economic features in a market with naturally fluctuating demand for electricity, and a variable/uncontrollable electricity supply from other sources (e.g., wind power).

2. Experimental method

A capsule method was employed to screen a number of materials for degradation under selected conditions of the SI and the Cu-Cl thermochemical cycles. The capsules operated at elevated pressure and temperature so that the phase composition of the working fluid replicated those expected in the actual process. Figure 2 shows the arrangement of phases and samples inside the capsules. The capsule wetted surfaces were all polytetrafluoroethylene (PTFE). For the testing relevant to the SI cycle (Figure 2a), a three-phase system was used: non-aqueous iodine liquid phase, liquid aqueous phase with sulphuric acid, and a gas phase consisting of vapours at equilibrium with the liquid phases under the test conditions. The testing for the Cu-Cl cycle (Figure 2b) employed two phases: aqueous concentrated hydrochloric acid phase (‘B’ in the drawing), and a gas phase (‘D’) at equilibrium with the liquid phase under the test conditions. The sample(s) (‘C’) were positioned so that they were in full contact with the simulated process working fluid. The identified shortcomings of the selected method included:

- lack of flow (conditions nominally stagnant but convection currents expected),
- relatively low sample to fluid ratio (taken into consideration in the assessment of results for samples that exhibited sufficiently high degradation rates),
- finite testing time in comparison to the time (about 10%) spent for capsule assembly/disassembly and under startup and shutdown transient from/to ambient to/from test conditions (assumed no degradation during transients),
- residual atmospheric oxygen possibly present (taken into account; virtually no effect expected because the systems were effectively redox buffered by the process chemicals),
- capsule leakage (discarded these results with volume change).

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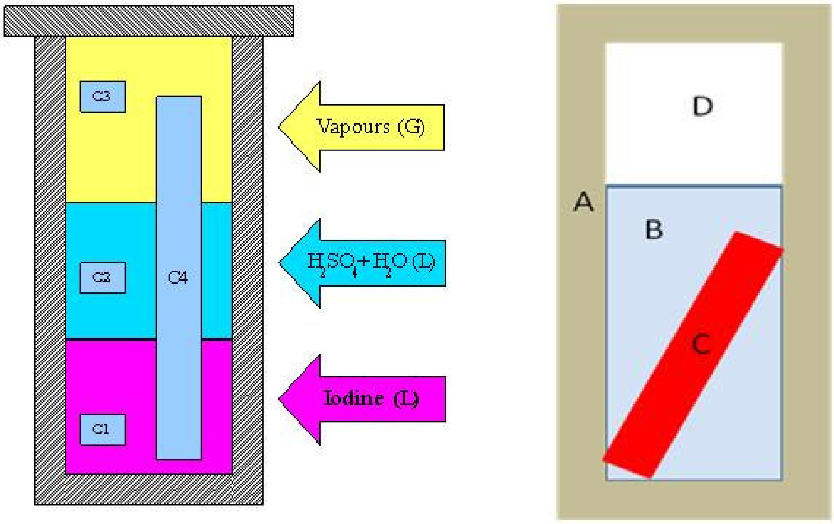
[1] CANDU® is a registered trademark of the Atomic Energy of Canada Limited.

It was concluded that, despite the shortcomings, the capsule method was suitable for screening of materials.



(a) (b)

Figure 2 Diagram of the phase and sample arrangement inside the capsules for testing under conditions of (a) the SI cycle ([1]) and (b) the Cu-Cl cycle.

Several combinations of temperature, pressure and composition of the simulated process working fluid were used, e.g., that suggested for the electrolyzer subsection of the Cu-Cl cycle: aqueous hydrochloric acid (13.6 mol/kg), copper(II) chloride (1.36 mol/kg) and copper(I) chloride (1.36 mol/kg) at 160ºC and 2.5 MPa (absolute). In some cases, a single fluid property was varied to assess its influence on degradation, e.g., the solution redox potential (by varying the Cu^{2+} to Cu^{+} ratio from 10:1 to 1:10). The details of the compositions of the test fluids are given in Table 1. The test temperatures were 150 and 180ºC for the SI cycle tests, and 80, 100, 125, and 160ºC for the Cu-Cl tests.

Table 1 Compositions of the test fluids

Identification	**Fluid composition**
SI-A	Mass %: 79.5 I_2; 2.0 H_2SO_4; 0.8 HI; 17.7 H_2O
CuCl-C1	mol/kg H_2O: 13.6 HCl; 1.36 CuCl; 1.36 $CuCl_2$
CuCl-C2	mol/kg H_2O: 13.6 HCl; 0.247 CuCl; 2.473 $CuCl_2$
CuCl-C3	mol/kg H_2O: 13.6 HCl; 2.473 CuCl; 0.247 $CuCl_2$

The materials tested included metals and engineering alloys, structural and functional polymers, elastomers, elemental-carbon based materials, ceramics, glasses, and composites. This is in line with the expectations that no single material will suffice to fully engineer a practical version of a complex system such as the Cu-Cl electrolyzer cell with the associated appendages and instrumentation. One of the criteria for the selection of the test materials was the “materials price index” described in detail in Reference [1]. This index, applicable to bulk materials for construction of heat exchangers, simultaneously considers the different relevant properties of the materials (the thermal conductivity, tensile strength, density, and the base price as a commodity material). Testing was also performed on several common engineering materials even though there was a likelihood that they might perform in a substandard manner under the simulated process conditions. Materials that obviously and rapidly failed were not investigated further.

Techniques employed to detect or quantify the degradation of the various materials, as well as to determine the mode of degradation when readily possible, included: visual examination, gravimetry, surface morphology by optical microscopy, dimensional examination, surface morphology by scanning electron microscopy (SEM), surface phase composition by X-ray diffraction (XRD).

For polymers exhibiting viscoelastic properties, the Portable Polymer Tester (PPT) was used to establish the change of the mechanical properties after the exposure to the corrosive environment in comparison with unexposed samples (identical material and geometry). The PPT technique, developed by Atomic Energy of Canada Limited, is described elsewhere, [3]. The typical test sequence consists of three parts: a preload and indentation phase, followed by a force relaxation phase, and a deformation recovery phase (Figure 3).

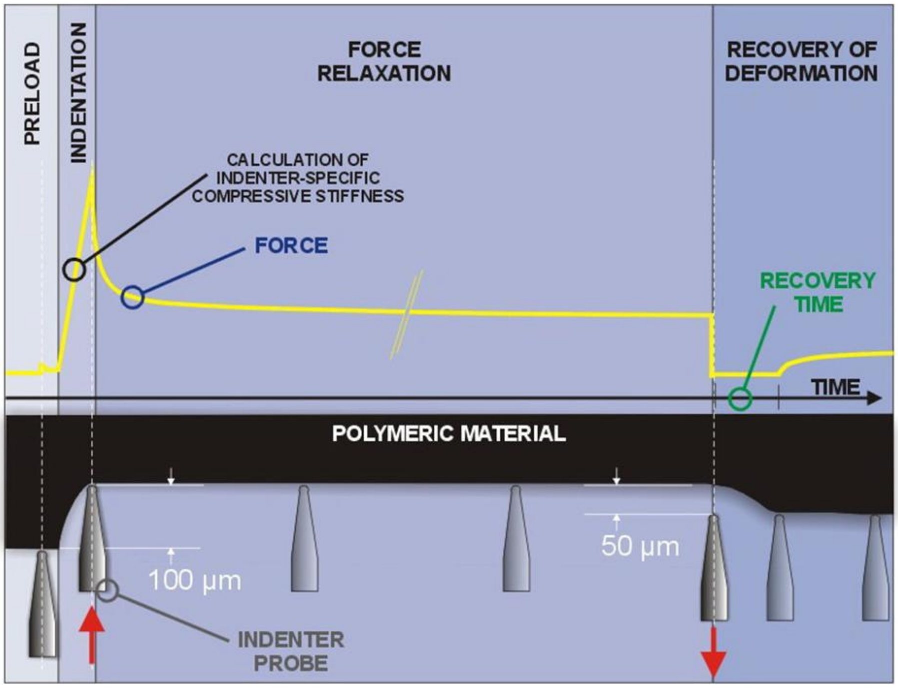


Figure 3 Illustration of the test sequence for the AECL Portable Polymer Tester

The indentation phase consists of driving the probe quickly into the polymer material to a pre-set indentation depth (set between 125 to 250 µm). Force and displacement signals measured simultaneously during this short phase are used to derive a material "compressive stiffness" that is specific to the indenter probe used.

The recovery phase starts at the end of the force relaxation phase. At this stage, the probe is retracted very quickly to a predetermined position and waits for the polymer surface to spring back and resume contact with the indenter tip. At that stage, a force is again detected by the load cell. The time between the retraction of the probe and the reappearance of a force on the indenter tip is defined as the polymer "deformation recovery time".

The compressive stiffness and the recovery time are reliable indicators of degradation of the viscoelastic properties of the tested materials [3]. The percentage of change in compressive stiffness and recovery time between a reference and a chemically exposed sample is a measure of the stability of viscoelastic properties for the tested materials under the test conditions.

3. Results

The details of the most recent experimental results are presented in Table 2 to Table 4. These results need to be taken as a supplement to the results obtained previously and reported in [1] and [2].

3.1 Polymeric Materials

Testing was performed on Kalrez®[2] and Norprene®[3] elastomers under varying temperature and redox conditions. The results are shown in Table 2. Kalrez (Table 2 Items 1 and 2) showed good dimensional and weight stability, in comparison with other fluoroelastomers tested previously under the same test conditions, [2]. The Norprene elastomer (Table 2 Items 3 to 10) showed a significant weight gain and linear dimension increase in the upper temperature range of its usability (125ºC). The weight gains reduced approximately linearly with decreasing exposure temperature (see Figure 4) within the range of the experimental conditions; however, notable gains could still be observed at test temperature as low as 80ºC. A sample of PTFE-based composite material (marked PTFE-3, Item 11 in Table 2) was tested and it showed a significant weight loss.

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[2] Kalrez is a registered trademark of DuPont Performance Elastomers L.L.C.

[3] Norprene is a registrated trademark of Saint-Gobain Abrasives Inc., Worcester, Ma, USA.

Table 2 Detailed experimental results for elastomers (7-d exposures)

Item	Material	Test identification	T [°C]	Fluid composition (see Table 1)	Mass change [%]	Observations
1	Kalrez	HS8-11	160	CuCl-C1	1.3	
2	Kalrez	HS8-12	160	CuCl-C1	1.4	
3	Norprene	HS5-1	125	CuCl-C1	38	Swelling, linear dimension increase by 3.5 to 12.5 % (depending on direction)
4	Norprene	HS5-2	125	CuCl-C2	31	Swelling, linear dimension increase by 2.5 to 10% (depending on direction)
5	Norprene	HS7-1	100	CuCl-C1	19	
6	Norprene	HS7-2	100	CuCl-C2	17	
7	Norprene	HS7-3	100	CuCl-C3	24	
8	Norprene	HS6-1	80	CuCl-C1	5.1	
9	Norprene	HS6-2	80	CuCl-C2	4.8	
10	Norprene	HS6-3	80	CuCl-C3	5.9	
11	PTFE-3	HS9-10	160	CuCl-C1	-7.5	No dimensional change observed despite a mass loss equivalent to thinning of 1.1 mm/a.

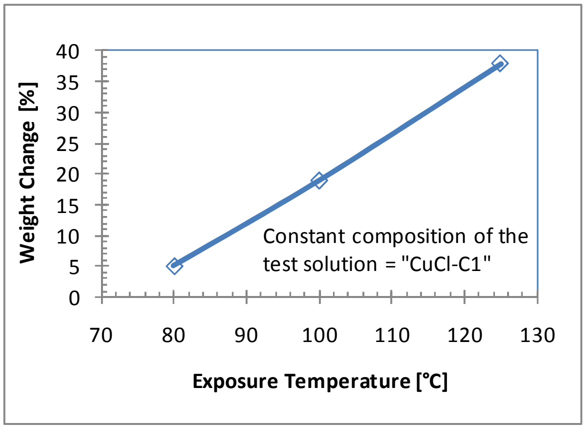

Figure 4 Weight gains as a function of exposure temperature for samples of Norprene® (the same test solution and an exposure time of 7 d).

The results obtained so far using the PPT technique are summarized in Table 3. The data show the change of polymer compressive stiffness and the recovery time on exposure to the test environment. Ideally, these parameters would not be affected at all by the polymer exposure to the test environment (i.e., 0% difference). The values recorded in Table 3 indicate no statistically significant change in the measured visoelastic properties for the Kalrez, and statistically significant changes for the Norprene sample after the 7-d exposure.

Table 3 PPT-measured change of the properties of elastomers after the 7-d test exposures

Item	Material	Test identification	Test temperature [°C]	Fluid composition (see Table 1)	Compressive stiffness [% change]	Deformation recovery time, [% change]
1	Kalrez	HS8-11	160	CuCl-C1	-2.7	+2.9
2	Norprene	HS5-1	125	CuCl-C1	-29	-27

3.2 Non-Polymeric Materials

Recent results for the corrosion testing of metal and alloy samples are detailed in Table 4. Titanium metal (marked Ti-1) and a titanium alloy (marked Ti-2) samples were found to corrode severely under the Cu-Cl conditions expected at the electrolyzer section, regardless of the redox conditions during the test. Also, two samples of gold metal were tested. No corrosion could be detected on the sample exposed to a moderately oxidizing environment (the ratio Cu^{2+} to Cu^{+} of 1). However, the same metal exhibited a weight loss equivalent to 2 µm/a under more oxidizing conditions at the ratio Cu^{2+} to Cu^{+} of 10. Additionally, two aluminium oxide-based materials were tested with highly variable results (Items 7 and 8 in Table 4). An example of the appearance of the coupons (before and after the exposure to the corrosive environment) is shown in Figure 5.

Table 4 Detailed experimental results obtained for non-polymer samples (7-d exposures)

Item	Material	Test Identification	T [°C]	Fluid Composition (Table 1)	Calculated Thinning Rate [mm/a]*	Mass Change [%]	Remarks
1	Ti-1	HS9-1	160	CuCl-C1	-5.6 (at least)	-100	Sample completely dissolved
2	Ti-1	HS9-2	160	CuCl-C2	-5.6 (at least)	-100	Sample completely dissolved
3	Ti-1	HS9-3	160	CuCl-C3	-5.6 (at least)	-100	Sample completely dissolved
4	Ti-2	HS9-4	160	CuCl-C1	-4.6 (at least)	-100	Sample completely dissolved
5	Au-1	HS9-7	160	CuCl-C1	-0.000	-0.04	Measured weight loss within the experimental uncertainty
6	Au-1	HS9-8	160	CuCl-C2	-0.002	-0.4	Error estimated at ±0.001 mm/a
7	Al_2O_3-1	HS9-5	160	CuCl-C1	-0.01	-0.04	No obvious signs of attack by visual examination.
8	Al_2O_3-2	HS9-6	160	CuCl-C1	-3.1	-9.8	The result may be less accurate due to the porous nature of the material. Degradation is apparent.
9	SiO_2-1	HS4-3	160	CuCl-C1	-0.003	-0.01	Error estimated at ±0.004 mm/a. No change apparent by visual examination.
10	SiO_2-2	HS9-9	160	Cu-Cl	0.00	0.00	No change detected.
11	SiO_2-1	ISC052	150	SI-A	not determined	not determined	Sample cracked.

** Negative numbers indicate mass loss; positive numbers indicate mass gain.*

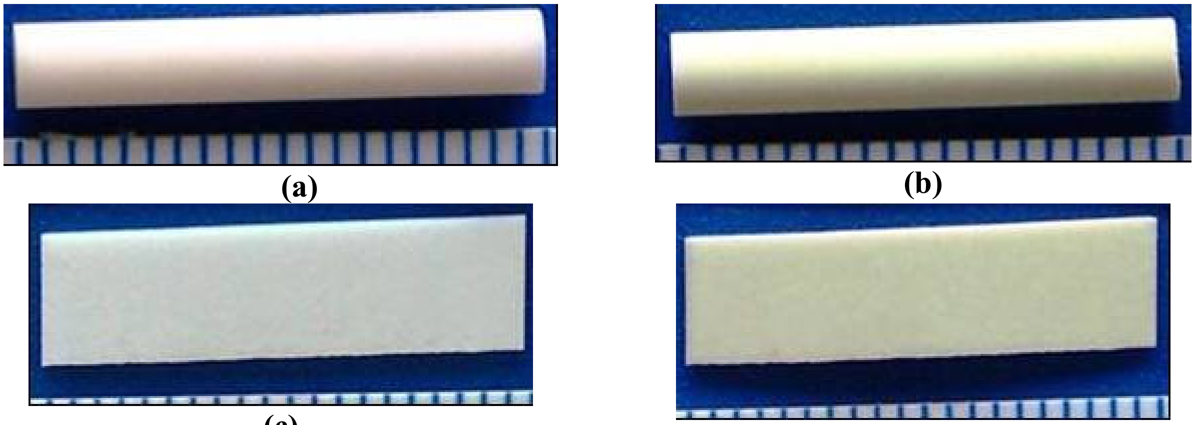
(a) (b)
(c) (d)

Figure 5 Example of the test coupons. (a) and (b): a sample of alumina-based ceramic (Item 8 in Table 4) before (a) and after (b) the exposure to a test environment; and (c) and (d): a sample of PTFE-based composite (Item 11 in Table 2) before (c) and after (d) the exposure.

Samples of fused quartz (silica) glass were exposed to the test conditions of Cu-Cl. The 7-d exposure at 160°C did not result in any detectable effect on samples of the quartz glass of two different commercial types of the glass (Items 9 and 10 in Table 4). This result can be contrasted with that of degradation obtained for the same type of quartz glass but under S-I conditions: degradation (Item 11 in Table 4). Figure 6 shows the quartz glass samples: the unaltered sample after the exposure to the Cu-Cl environment and the sample degraded on exposure to the SI test conditions.

(a) (b)

Figure 6 Silica glass samples after an exposure to (a) the Cu-Cl test environment and (b) the SI test environment (Items 9 and 11 in Table 4).

4. Discussion

4.1 Polymers

Testing under the conditions relevant to the Cu-Cl cycle has been performed for several grades of elastomers (see [2] for the results for the grades of elastomers tested previously). Generally, the elastomers tested all exhibited mass gain and swelling, but to a varying degree. These have been interpreted as an uptake of the working solution into the volume of the elastomer. Note that the test exposure was performed under unrestricted access of the working fluid to all the surfaces of the elastomer. Therefore, the same elastomers may exhibit lower uptake rates when mass transfer is restricted under the conditions of application of the elastomers for sealing. The dimensional changes appear to be the most problematic immediate effect of the elastomer coupons to the corrosive environment. For the most degradation resistant elastomers available on the market, the changes in the viscoelastic properties, if any, appear manageable under the test conditions. The best elastomer material tested to date at the conditions of the electrolyzer of the Cu-Cl cycle is Kalrez.

The permeability of polymers to the working fluids was not an object of this investigation. However, some permeability-related effects were encountered which appear relevant to the degradation of materials if PTFE components or coatings were to be employed. Two of these effects were related to the application of the PTFE capsules shown in Figure 2. The effects can be summarized as follows:

- Permeability of PTFE to iodine was visually observed, as reported previously ([1], Figure 8).
- Permeability of PTFE to HCl under Cu-Cl conditions can be inferred from occasional "bulging" of the PTFE capsule (Figure 7). The bulging was coupled to localized corrosion of the high-nickel alloy material in the spot underneath the bulge, while the PTFE maintained its continuity (no breakage). However, alternative explanations for the observed bulging cannot be excluded.
- Mass loss of the sample of PTFE-based composite material (Item 11 in Table 2, and Figure 5c and d) can also be attributed to either the permeability of PTFE matrix of the composite under the test conditions, or perhaps residual porosity of the filler material (nominally glass).

(a) **(b)**

Figure 7 Experimental evidence of permeation through the PTFE capsule wall: (a) Iodine staining in the bulk of the PTFE under SI cycle conditions [1]; and (b) a "bulge", visible inside a PTFE test capsule correlating with localized corrosion underneath under Cu-Cl cycle conditions.

The currently recommended polymer materials for the application in the Cu-Cl cycle electrolyzer are: PTFE, Kalrez, and PEEK ([2]). Additional work with polymers under Cu-Cl conditions is still being performed.

4.2 Platinum and gold

Platinum samples were tested under a number of conditions, both for the SI and Cu-Cl cycle. Measurable mass changes (variably gains or losses) were recorded for Pt under the SI conditions, while the mass changes under the Cu-Cl conditions were all within the limits of uncertainty of the experimental method. Under the SI conditions, the initially shiny Pt metal surface was found after testing to be covered with non-uniform, in places thick (up to about 50 µm) and non-adherent deposits. In one test under the SI cycle conditions, which was performed in the presence of vanadium, a Pt metal sample dissolved completely implying corrosion at a rate in excess of about 3.8 mm/a. No surface morphology changes were detected on the Pt samples in tests under the Cu-Cl conditions.

Gold samples were also tested under a number of conditions. In tests under SI conditions the weight changes for Au were greater than those for Pt. Microscopy was conducted on the samples after the tests; the Au metal surface appeared etched or re-constructed. It has been concluded that gold was not inert or passive under the SI test conditions. In contrast, under Cu-Cl conditions, the Au samples appeared unaffected, except for a small mass loss (equivalent to about 2 µm/a ± 1 µm/a) recorded in a test under the highest redox potential and the highest temperature employed.

In tests in which degradation was detected, this occurred predominantly in the liquid phases. No degradation at elevated rates was noted at the interfaces between the test fluids under the SI cycle conditions (see Figure 2 for the two interfaces present in the tests).

In summary, the results indicated no attack on Pt metal under the range of Cu-Cl conditions tested. It has been concluded that surface plating with Au for corrosion protection can be useful at those locations of the Cu-Cl cycle where very high redox potentials do not exist under the process conditions. However, generally, the results indicated that corrosion resistance of platinum and gold metals cannot be taken for granted under the oxidizing redox conditions possible in some locations in the SI and Cu-Cl cycles and in the presence of high concentration of halides, in the temperature range tested. Vanadium can be a corrosion accelerator under SI conditions tested.

4.3 Tantalum and its alloys

Several samples of tantalum and tantalum alloys with tungsten and niobium were tested. Under SI conditions, significant attack was detected in only one test, which was conducted in the presence of vanadium. This result was reminiscent of that for the sample of Pt, described in the previous section. These two results taken together suggest that vanadium can enhance corrosion under the SI conditions investigated (vanadium is known to be corrosive).

In the balance of tests under SI cycle conditions, the measured mass losses for Ta and its alloys were all generally below the limits of resolution of the experimental method which was always substantially below 0.1 mm/a. Thin surface oxides (light interference patterns) were observed on the samples surfaces after the tests, and no cases of localized attack were detected by optical or SEM microscopy, indicating passivity of Ta and its alloys tested under the SI test conditions.

Similarly, under the Cu-Cl conditions tested, Ta and its alloy with tungsten did not exhibit degradation at a rate that could be detected either by mass loss, dimensional change or by surface morphology. However, an alloy of Ta with 40% Nb experienced corrosion at a rate of about 0.7 mm/a, which is considered sufficiently high to disqualify the alloy from major applications under Cu-Cl cycle conditions. It can be noted that corrosion is not only a material integrity issue, but is expected to affect performance of many components in a closed cycle by fouling.

In summary, experimental results indicate that Ta and Ta-W alloys tested are suitable candidates for the construction materials for both the Cu-Cl and SI cycles as far as their corrosion behaviour is concerned. The main known drawback of Ta and its alloys is the cost, estimated previously using the "cost index" (for heat exchanger application) to be about 23 times higher than that of stainless steel [1]. Workability is also sometimes an issue encountered in application of Ta alloys.

4.4 Titanium and zirconium

Tests were conducted with several titanium and zirconium metals (pure) and alloys. See [2] for the results for Zr-based materials. It is evident that neither Ti nor Zr-based materials are suitable for application under the Cu-Cl electrolyzer conditions with aqueous HCl and water-dissolved copper salts.

5. Conclusions

Selection of materials is one of the major challenges for implementation of thermochemical cycles for hydrogen production for the future hydrogen economy. This paper presents a summary of the results of an experimental investigation to screen selected materials for degradation under selected conditions of the sulphur-iodine (SI) and copper-chlorine (Cu-Cl) thermochemical cycles. Partial results, with many pertinent details, were presented previously ([1], [2]). This paper gives additional experimental results and attempts to summarize the useful conclusions reached to date on the basis of the experimental data.

Experimental results for several polymers are given. Kalrez appears to be the most usable elastomer tested to date under the conditions of the electrolyzer for the Cu-Cl cycle. Other polymers useful under the Cu-Cl cycle conditions are PTFE and PEEK [2]. When employing PTFE in the SI and Cu-Cl cycles, it is important to consider the permeability of PTFE to the components of the working fluid. Surface plating with Au for corrosion protection can be useful at those locations of the Cu-Cl cycle electrolyzer where very high redox potentials do not exist under the process conditions. However, generally, the corrosion resistance of Pt and Au cannot be taken for granted at those locations of the SI and Cu-Cl cycles where high redox potentials are expected. Experimental results indicate that Ta and Ta-W alloys tested are good candidates for the construction materials for both Cu-Cl and SI cycles as far as their corrosion behaviour is concerned. Vanadium has been identified as a factor in the loss of passivity of Ta alloys and Pt under SI conditions. Titanium and zirconium metals are inappropriate for application under Cu-Cl cycle electrolyzer conditions at elevated temperature and pressure.

6. References

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