DEGRADATION OF MATERIALS UNDER CONDITIONS OF THERMOCHEMICAL CYCLES FOR HYDROGEN PRODUCTION[1]

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Abstract

A capsule method has been developed and employed to measure the degradation rates of selected materials under some of the most challenging conditions relevant to the sulphur-iodine (SI) and the copper-chlorine (Cu-Cl) thermochemical cycles for hydrogen production. The materials tested so far include metals and engineering alloys, structural and functional polymers, elastomers, carbon-based materials, ceramics and glasses, and composites. A number of characterization methods have been used to detect and quantify the degradation of the diverse materials and, when feasible, establish the mode of attack.

The paper details the results of this ongoing experimental investigation. The investigation currently focuses on the copper-chlorine hybrid cycle. The environment representative of the conditions in the electrolyser subsystem was approximated with an aqueous solution of hydrochloric acid (13.6 mol/kg), copper(II) chloride (1.36 mol/kg) and copper(I) chloride (1.36 mol/kg) at 160°C and 2.5 MPa (absolute). The current (tentative) recommendations for the selection of the materials required for the construction of the electrolyser subsystem of the copper-chlorine hybrid cycle, and the associated rationale, are presented and discussed.

Keywords: Material, Corrosion, Degradation, Copper-Chlorine Cycle

1. Introduction

A hydrogen production thermochemical cycle is a hydrogen manufacturing process in which the overall net reaction is that of the decomposition of water into hydrogen and oxygen (Figure 1). Numerous thermochemical cycles have been proposed as potential pathways to the future “hydrogen economy”. Hydrogen economy is a vision for the widespread use of hydrogen as a fuel. It would eliminate fossil fuel use for many industrial and transportation applications and reduce greenhouse-gas emissions, while retaining access to a portable source of energy with high energy density. The energy would be clean because burning hydrogen produces just water. The hydrogen economy would also be sustainable, in contrast to petroleum. A future CANDU®[2] power plant could serve as the source of energy (heat, or heat and electricity) for the production of hydrogen to drive the hydrogen economy.

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[1] AECL Report (CW-122820-CONF-003)

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

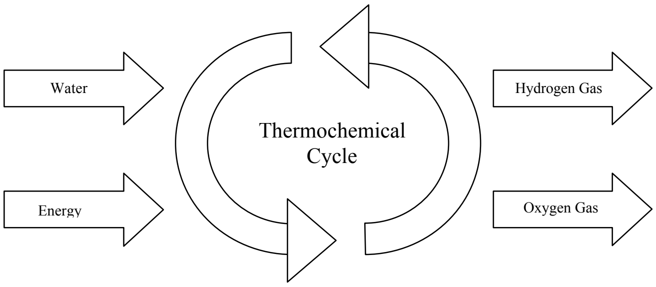

Figure 1 A Thermochemical Cycle for Water Splitting.

Previously [1], AECL performed work on materials degradation using the sulphur-iodine (S-I) thermochemical cycle. The current work is a continuation of the previous project, using a similar experimental method, but with the emphasis shifted towards another promising cycle, the copper-chlorine (Cu-Cl) cycle [2]. The Cu-Cl cycle is suitable for hydrogen co-generation in supercritical water-cooled reactors (SCWR) operating at about 650°C.

The Cu-Cl cycle utilizes a series of reactions of compounds of copper (in varying states of oxidation) and hydrochloric acid. With the exception of water, hydrogen and oxygen, all chemicals are completely recycled within the Cu-Cl process, hence the consideration of the cycle for large-scale production of gaseous hydrogen with the utilization of nuclear heat sources. The cycle uses heat; therefore, it is termed “thermochemical”. A variant of the process that incorporates an electrolytic step is called a “hybrid” cycle. A hybrid Cu-Cl cycle is currently under development in Canada, at the University of Ontario Institute of Technology (UOIT), Oshawa, Ontario, with a contribution from the Atomic Energy of Canada Limited (AECL). This work is part of the collaborative effort. The AECL contribution reported in this paper focuses on selection of materials for the electrolyser section of the Cu-Cl cycle.

2. Objective and Scope

The technical objective of this work is to screen materials for degradation under conditions of thermochemical cycles for hydrogen production from nuclear energy. The materials selected for testing in the work described in this paper are those that are considered for construction of the electrolyser cell of the hybrid Cu-Cl cycle, and of the associated components. The test conditions are relevant to the anticipated process conditions in the electrolyser.

The technical challenge is that the environments are highly corrosive: a concentrated aqueous solution of hydrochloric acid and copper salts, elevated temperatures and pressures, and variable redox conditions of the reacting system. The literature corrosion data for hydrochloric acid are not necessarily applicable because redox conditions are altered by the presence of the copper ions.

The work is ongoing and this paper describes the initial experimental results.

3. Experimental Method and Materials

The previously developed capsule method [1] was used to expose the coupons to a test solution with a selected initial composition for a prescribed period of time at a specified temperature. This capsule method previously proved to be suitable for rapid screening of materials for degradation under some of the most corrosive conditions of the SI cycle: a multi-phase system containing water, sulphuric acid, iodine and hydroiodic acid; and three phases (aqueous, molten iodine, gaseous). The method was adapted to the conditions of the Cu-Cl cycle electrolyser (different temperature, pressure, and composition of the fluid).

The capsules employed in the current investigation were cylindrical with internal dimensions of 10.4 mm diameter x 60 mm length. The capsule material in contact with the working fluid and with the samples was exclusively PTFE polymer. Therefore, galvanic coupling or transfer of the corrosion products from the capsule wall to the sample was not an issue. Alternative materials considered for the capsule ("Macor" glass and a zirconia-based ceramic) failed under the process conditions and were not used in the subsequent tests.

The test principle employed was similar to that described in [3], with the limitations arising from the small size of the capsules used in this project[3]. Each capsule contained 3.0 grams of the test solution and a single coupon completely submerged in this solution (Figure 2). During the tests, the capsules were positioned "vertically" to assure that the coupons remained entirely submerged in the liquid phase. The initial composition of the test solution was: 13.6 mol/kg HCl, 1.36 mol/kg CuCl, and 1.36 mol/kg $CuCl_2$. This composition is considered to be an approximation of the future process conditions in the electrolyzer middle part.

The high concentrations in the solution assured a large stoichiometric excess of acid with respect to the coupon material for the most likely degradation reactions. The only possible exceptions were the largest coupons used in this investigation if they exhibited the exceptionally high degradation rates (e.g., 10 mm/year). The capsule method is suitable for the screening of materials because it is considered to be accurate for coupons exhibiting low degradation rates (as long as the accumulation of the corrosion products in the capsule solution does not inhibit further corrosion).

All solutions were prepared using reagent-grade chemicals and deionized water.

The tests were conducted for 168 h (7 d) at a temperature of 160°C and a pressure of 2.5 MPa (absolute). During the test, the capsule was sealed and the fluid inside the capsule was nominally stagnant (some convection currents were expected). A gentle heat up and cool down was pre-programmed to avoid excessive stresses on the capsules and potential leakage. No significant leakage was confirmed by assessing the amount of the fluid at the end of each test. The total time of heating, cooling, and capsule preparation time added up to about 6 h of coupon-liquid contact time at variable temperatures from ambient up to 160°C. This was not counted as part of the test time. Thus, the relative uncertainty of the test time was estimated to be +4%.

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[3] Reference [3] suggests 0.2 mL (or more) of test solution per 1 mm² of metal sample.

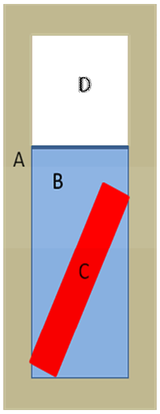

Figure 2 Schematic of the arrangement of the coupon inside the capsule.
A: Capsule; B: Test Liquid; C: Coupon; D: Vapour Space.

For the initial testing reported here, the materials needs for the construction of the following components of the Cu-Cl cycle have been considered:

- the electrolyser vessel, including its closure,
- the electrolyser cell internals, and
- the electrolyser appendages, e.g., inlet and outlet piping, pump(s), heat exchanger(s), instrumentation, etc.

The test coupons were prepared from pure and commercial materials. The materials tested so far include pure metals and engineering alloys, structural and functional polymers, elastomers, carbon-based materials, ceramics and glasses, and composites. Samples of the selected materials were obtained in one of the following forms: foil, sheet, wire, small-diameter rod, or small-diameter tube. The form of the material was selected based on the commercial availability and so as to maximize the ratio of coupon surface area/coupon mass. From this stock material, several identical corrosion coupons were prepared. The metal coupons were finished to a surface roughness (arithmetic average) of ≤ 1 µm. A typical coupon had a mass of 0.4 g and a geometrical surface area of 175 mm^2 (although the mass and sizes varied from material to material, depending on the initial form used). The coupons were thoroughly washed using an ultrasonic bath, first in water, then by methanol, then carefully dried to a constant weight and subsequently stored in a dessicator. The following materials have been tested so far:

- PTFE polymer (polytetrafluoroethylene) (a commercial grade)
- PEEK polymer (polyetheretherketone) (3 different commercial grades)
- Viton fluoroelastomer rubber (2 different commercial types, "Viton®[4]")
- Nafion®[5] (2 grade, proton exchange/conducting membrane,)

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[4] Viton is registered trademark of DuPont.
[5] Nafion is a registered trademark of DuPont.

- Graphite plate (extruded grade)
- Graphite plate (as above but resin-impregnated)
- Toray®[6] carbon-fiber paper
- Toray carbon-fiber paper (as above but Teflon impregnated)
- Alloy 625 (UNS N06625; Ni-21Cr-9Mo-5Fe-3.5Nb-1Co)
- Alloy B2 (UNS N10665; Ni-28Mo)
- Alloy C22 (UNS N06022; Ni-22Cr-13Mo-3Fe)
- Pt metal (B561-94 Grade 99.95)
- Zr metal (non-nuclear grade, > 99% Zr+Hf, B-550-07 R60702, Zr-1.6Hf)
- Alloy Zr-4 (Zircaloy-4, nuclear grade, Zr-1.6Sn)
- Ta metal (pure)
- Alloy Ta-2.5W
- Alloy Ta-40 Nb
- Nb metal (pure)
- SiC, silicon carbide commercial ceramics
- YSZ, yttria-stablized zirconia commercial ceramic
- Macor®[7] ceramic (mica in borosilicate glass matrix)

The identification of the coupons follows their naming in the list above. Additional materials are currently being selected based on the initial results. To quantify the degradation, the following techniques are being applied: the mass change of the coupon (accuracy of 0.0001 g), linear dimension change, microscopy (scanning electron and optical microscopy to detect localized corrosion and modes of attack) and, for elastomers and some polymers, examination of the change in mechanical properties. The mass change was recorded without descaling, but after thorough washing of the coupons, first with hydrochloric acid (to remove any traces of copper salts), then distilled water, followed by methanol and then drying to a constant mass. The mass change expressed as % of the initial mass is given for polymer samples that appear to be affected by the exposure to the corrosive liquid in their entire volume. The thinning rate was calculated from the mass change for other coupons, based on the sample geometric surface area (i.e., disregarding surface roughness or porosity for porous samples). All handling of the coupons was performed exclusively with plastic forceps.

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[6] Toray Industries Inc. The paper is made of their Torayca® carbon fibre.

[7] Macor is a registered trademark of Corning Inc.

4. Results and Discussion

Example views of coupons after the capsule exposure, alongside with unexposed coupons ("blanks"), are given in Figure 3. The results to date are summarized in Table 1. The surface analysis of the coupons is still ongoing; therefore, all the results are preliminary.

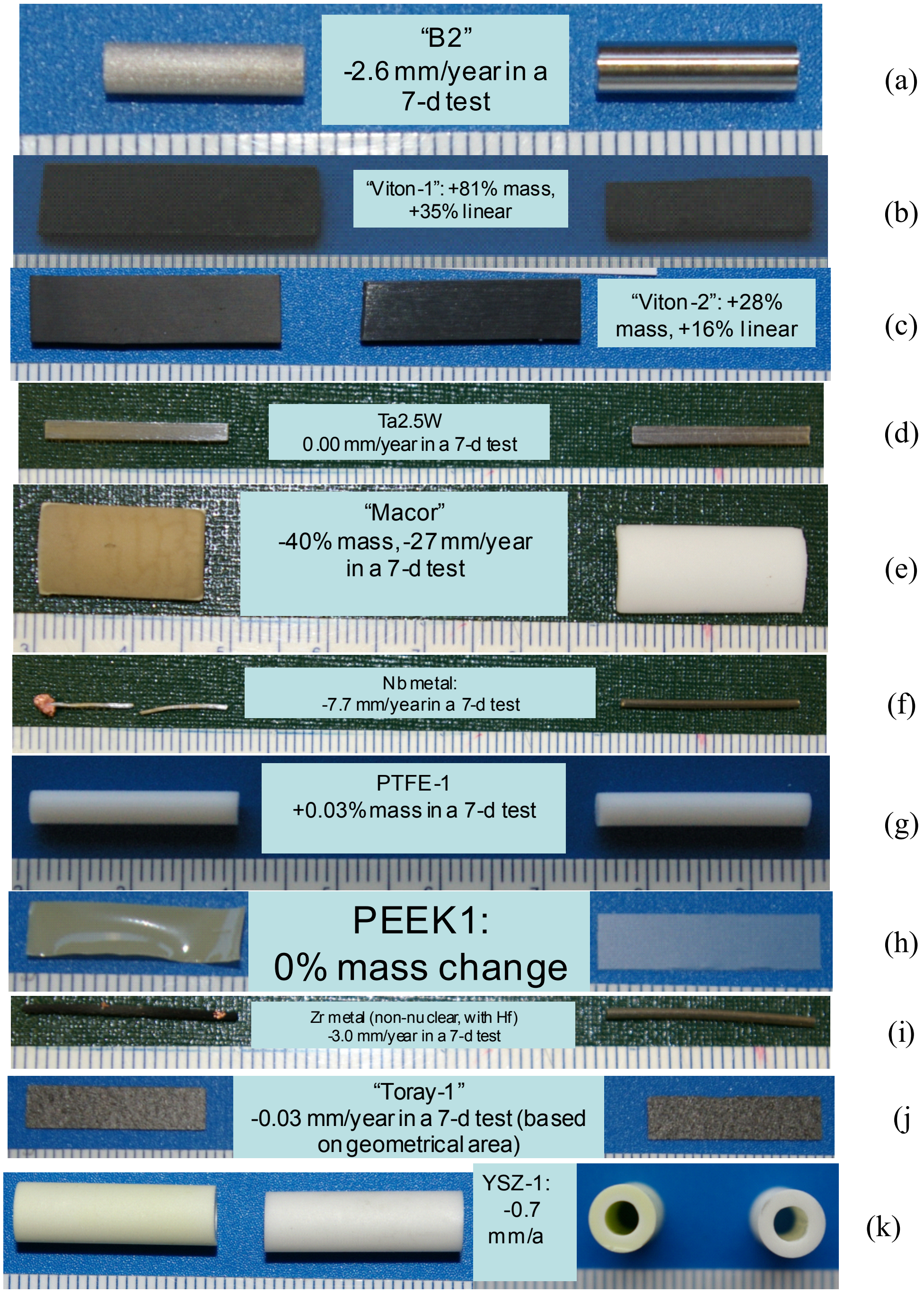

Figure 3 Example views of the blank coupons "before" (right) and test coupons after (left) the capsule exposure

	Material Identity	**Test Identification**	**Calculated Thinning Rate mm/year**	**Mass Change %**	**Absolute Uncertainty in the Mass Change %**	**Observations**
1	PTFE-1	HS1-2	*	+0.03	±0.03	
2	PEEK-1	HS2-5		0	±1	
3	PEEK-2	HS4-5		+0.70	±0.01	
4	PEEK-3	HS4-6		+0.63	±0.01	
5	VITON-1	HS1-1		+81	±0.1	Swelling, linear dimension increase by 35%
6	VITON-2	HS4-9		+28.4	± 0.03	Swelling, linear dimension increase by 15.6%
7	NAFION-1	HS4-2		0.00	±1	
8	TORAY-1	HS2-4	-0.03	-1.3	±1.3	
9	TORAY-2	HS3-1	0.00	0.00	±1	
10	GRAPHITE-1	HS4-7	0.00	0.0	±0.5	
11	GRAPHITE-2	HS4-8	+0.10	+0.9	±0.4	
12	Pt (metal)	HS1-3	0.00	0.00	±0.5	
13	Alloy 625	HS1-4	-10.6 (at least)	-100	±0.11	Coupon completely dissolved
14	Alloy B2	HS2-1	-2.6	-6.6	±0.01	
15	Alloy C22	HS2-2	-17.4	-47	±0.02	
16	Alloy Ta-2.5W	HS3-3	0.00	0.00	±0.01	
17	Alloy Ta-40Nb	HS3-4	-0.72	-0.8	±0.008	
18	Ta (metal)	HS3-4	0.00	-0.04	±0.04	
19	Nb (metal)	HS3-7	-7.7 (at least)	-59	±0.1	Large cluster of copper deposit at the bottom of the sample.
20	Zr (metal, non-nuclear)	HS4-1	-3.0 (at least)	-25	±0.1	Small islands of copper deposits visible.
21	Alloy Zr-4 (nuclear)	HS3-8	-16.2 (at least)	-100	±0.04	Coupon completely corroded, solid corrosion products visible
22	SiC ceramic	HS2-6	0.00	0.00	±0.02	
23	Macor glass	HS3-4	-27	-40	±0.04	Color changed from white to yellow. Granulation visible after the test.
24	YSZ ceramic	HS4-4	-0.7	-1.8	±0.01	

* *A blank cell signifies that the value is not reported because it is not believed to be physically meaningful.*

Table 1 Experimental results.

From the results presented in Table 1, the following materials exhibited a degradation rate sufficiently high that their practical application under the test conditions appears unlikely: Alloy 625, Alloy B2, Alloy C22, Alloy Ta-40Nb, Nb (pure metal), Zr metal (non-nuclear grade, with hafnium), Alloy Zr-4 (nuclear grade, Zr-1.4Sn, no hafnium), Macor glass (mica in borosilicate glass matrix), and YSZ ceramic.

Metallic copper deposits were detected on the zirconium and niobium metal coupons after the capsule exposure (see Figure 3(f) and (i)). The mass change was recorded without the removal of these firmly attached copper deposits. Should the copper metal deposits be removed from the corroded coupons, then the calculated metal loss rate would be greater. However, the uncertainty in the calculated rate of thinning associated with the presence of the copper metal deposit does not affect the clear conclusion that the Zr and Nb materials tested appear unsuitable for service under the test conditions.

PTFE and PEEK in their pure form appear, within the experimental uncertainty, unaffected by the exposure to the test conditions for seven days as far as mass and macroscopic dimension were concerned. However, two commercial grades of PEEK did exhibit some mass gain; while a thin foil exhibited shape and colour change. The work with PEEK and other polymers under Cu-Cl electrolyser conditions is ongoing. The PTFE and PEEK polymers are currently among the best candidate materials for the application in the Cu-Cl electrolyser at elevated temperatures. The potential limitations related to the application of polymers like PTFE is their tendency to stress crack under conditions similar to those encountered in the Cu-Cl cycle electrolyser [4] and a relatively high permeability of polymers to fluids [5].

Two grades of the Viton fluoroelastomer have been tested so far. Both exhibited significant mass gains and increase in linear dimensions ("swelling", see Figure 3(b) and (c)). Mechanical testing of polymers and elastomers (changes of mechanical properties due to the capsule exposure) is currently being performed using an AECL-developed experimental "Portable Polymer Tester". However, the effect of the exposure on the foil proton-conducting properties has not been assessed so far.

Nafion proton conducting resin appeared to be relatively unaffected by the exposure to the test conditions, except for the shape of the thin foil, which could not be maintained under the test conditions.

Four different elemental carbon-based samples were tested so far. Only one sample exhibited a mass change (gain) beyond the experimental uncertainty. This commercial material, currently used in the ambient-temperature electrolysis cell, contains commercial graphite impregnated with a resin. The (small) mass gain is likely attributable to the resin. Graphite-based materials with no resin appeared unaffected by the capsule exposure.

Tantalum metal and a tantalum alloy with tungsten (2.5%W) did not exhibit measurable corrosion under the test conditions. Ta-2.5W is clearly suitable for application under the test conditions if a metal is necessary. However, its application is expected to be limited because of its high cost (quantified previously for a heat exchanger application[8] to be about 23 times that for stainless steel [1]. An alloy of tantalum with niobium, which would be significantly less expensive [1], corroded at an unacceptable rate.

The mass change of the sample of a silicon carbide ceramic was below the experimental uncertainly. Silicon carbide tubing could be valuable for heat exchanger applications. However, the possibility of release of silica into the solution may limit its usability. Note that also glass is expected to thin at a non-negligible rate under the hydrothermal conditions of the Cu-Cl cycle electrolyser.

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[8] Only the cost of the materials, at a commodity price, and their physical properties (the tensile strength, thermal conductivity, density, etc.) were accounted for. The number given does not include the (likely) increased cost of the engineering and manufacturing of tantalum parts.

5. Conclusions

A series of measurements of degradation rates of materials was conducted under conditions representative of the Cu-Cl cycle electrolyser section. From the measurements completed to date, the following materials may be suitable for the application inside the electrolyser: PTFE polymer, PEEK polymer, Ta-2.5W alloy, Ta metal, Pt metal, Nafion proton conducting resin, Toray carbon-fiber paper, commercial graphite, and commercial silicon carbide ceramic. Known issues for these materials under the test conditions include high price of tantalum, stress cracking of PTFE, relatively high permeability of polymers to fluids, and possible release of silica to the solution by the SiC ceramic. The following materials exhibited degradation rate sufficiently high that their application under the test conditions appears unlikely: Alloy 625, Alloy B2, Alloy C22, Alloy Ta-40Nb, Nb metal, Zr metal (non-nuclear grade with hafnium), Alloy Ziracaloy-4 (nuclear, Zr-1.4Sn), Macor ceramic (mica in borosilicate glass matrix), and YSZ ceramic.

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7. References

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