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OPTIMIZATION OF MICRO-CHANNEL FEATURES IN A CERAMIC HEAT EXCHANGER FOR SULFURIC ACID DECOMPOSITION

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ABSTRACT
It has been proposed that compact ceramic heat exchangers can be used for high temperature, corrosive applications. This paper discusses the development and optimization of a micro-channel heat exchanger for the decomposition of sulfuric acid as part of the hydrogen producing Sulphur-Iodine (SI) thermo-chemical cycle. The optimization process combines thermal-hydraulic and structural modelling, materials testing, component fabrication and performance testing. Based on a shell and plate design, modular stacks of microchannel containing plates form the primary heat exchange surfaces in a compact arrangement. These modules enable scaling to commercial-scale processes; the microchannels enhance the heat transfer while maintaining low pressure drops within the system. The ceramic materials provide for long-life applications. The feasibility of this compact heat exchanger was assessed through thermal and mechanical models and by flow testing of as-fabricated components. The results of this design effort with its associated performance goals and development status will be reported.

INTRODUCTION
Several versions of thermo-chemical water splitting processes were developed in the 1970's[1,2]. The motivation for these processes is that water can be thermo-chemically split generating hydrogen with an estimated thermal efficiency greater than 50%[3]. Key to these processes is the decomposition of sulfuric acid that occurs in multiple reactions. These endothermic reactions are driven by utilizing high temperature waste heat (as in a nuclear power plant or solar collector) ranging from 450C to 900C[4]. The realization of these processes requires the implementation of high temperature, corrosion resistant heat exchangers.

Over the last 30 years significant advancements have been made in heat exchanger technology. Compact heat exchanger technology that reduces the length scale at which heat and mass transfer occur has enabled high efficiency heat exchangers[5]. In metal alloys these compact heat exchangers are used in car radiators[6], petrochemical processing[7] and HVAC[6]. The introduction of super-alloys into these compact heat exchangers has defined the current state of the art for high temperature heat exchangers.

However, even these super-alloys do not have sufficient material and mechanical properties for the sulfuric acid decomposition process[8,9,10,11]. Sandia National Labs has been chartered to develop an experimental test loop wherein materials and sub-scale components can be evaluated. Their findings showed that the super-alloy components showed rapid visible corrosion[12]. A Japanese energy consortium is investigating the development of this process and has determined to use high temperature ceramics (silicon carbide) for their demonstrations[13]. The activity of these environments is too corrosive and the high temperatures promote excessive creep even for super-alloys.

Significant research was also done in last several decades to develop ceramic components for higher efficiency gas turbine cycles[14]. In these applications, temperatures approach 1000C in vitiated air environments. Extensive corrosion studies investigated the durability of the ceramic materials in mixed steam, oxygen and combustion environments. These finding suggest that for many applications, such as combustors and based gas to gas recuperators, these materials corrode passively and have sufficiently low recession rates for durable operation[15]. The commercialization of these high temperature ceramic components has been derailed by their economic performance verses their technical performance[16].

This paper discusses the design of a compact heat exchanger using high temperature, corrosion resistant ceramic materials as applied to the decomposition of sulfuric acid in the sulfur iodine thermo-chemical cycle (see Figure 1). This design builds upon the work done in metallic heat exchangers and ceramic materials development. The coupling of these technologies and advanced manufacturing methods has enabled the development of corrosion resistant, high temperature heat exchangers as reliable, efficient, cost effective alternatives for severe environments.

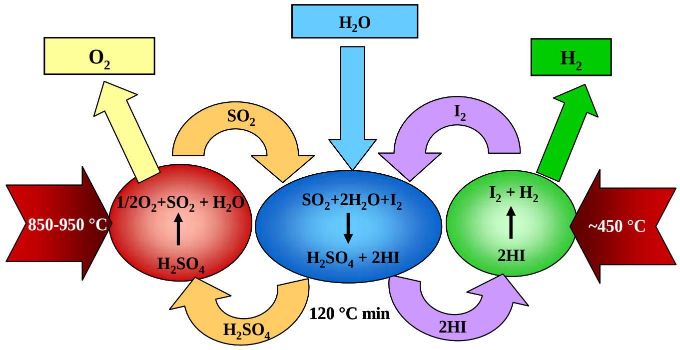

Figure 1. Simplified Sulfur Iodine Cycle

DESIGN AND OPTIMIZATION APPROACH

The predominance of the shell and tube heat exchanger in the process industry speaks to its cost effectiveness and overall reliability. However, when high temperature corrosive environments are required, compact heat exchanger designs can reduce in-process inventory, minimize expensive materials and heat exchanger effectiveness leading to a more economical system with improved lifetimes. Hence as a design premise, a “shell and plate” design was adopted wherein the primary heat transfer surfaces of a shell and tube design were replaced with high surface area modular stacks of plates. Figure 2 illustrates how this design is adapted to the sulfuric acid decomposition process.

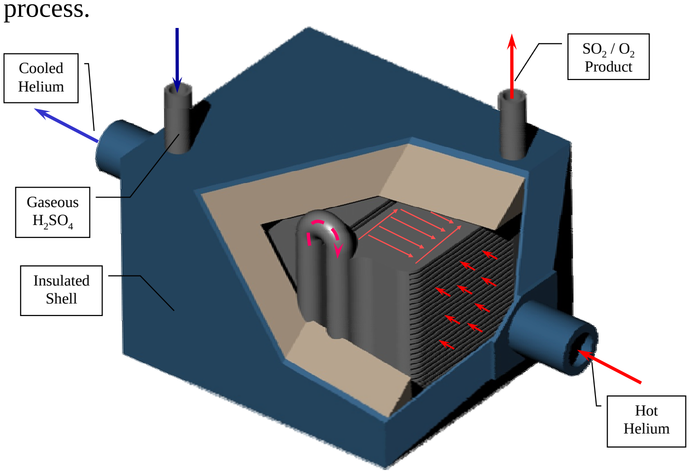

Figure 2. Shell and Plate Design of a Compact Heat Exchanger

Given this basic concept, the design and optimization of this high temperature heat exchanger has been based on multiple facets of development. These are:

1) materials selection,
2) engineering models to predict thermal performance and mechanical stress/reliability models,
3) design for manufacturing constraints for components and assemblies, and
4) experimental validation of as-fabricated components.

MATERIALS SELECTION

In investigating materials of construction for the SI process in the late 1970’s, preliminary corrosion experiments were made by Irwin et al.[11] Their experiments exposed many materials to hot concentrated sulfuric acid for 1000 hours. By ranking the corrosion durability of these materials, it was determined that most metal materials were inferior to ceramics. These results are summarized in Table 1.

Table 1. Exposure Hours Endured for Candidate Materials in H_2SO_4 at 361C.

Material	Hours	Material	Hours
Silicon Nitride (Reaction Bonded)	1000	Tantalum (preanodized)	250
Silicon Nitride (Hot Pressed)	1000	SS 18-18-2	521
Duror Acid-Proof Brick	1000	SS 310	521
Macor Ceramic	1000	Inconel 625	500
Silicon (Polycrystal)	1000	Alonized Inconel 625	500
Durichlor 51	1000	Sialon 80	500
Duriron	1000	Sialon 81	500
Silicon Carbide-CVD	1000	Sialon 88	500
Vitreous Carbon	1000	Cartech Type 20Cb3	500
Alumina	1000	Hastelloy G	500
Aluminum Silicate	1000	Carbon Steel (CS) 1018	500
Hastelloy C-276	750	Alonized CS 1018	500
Incoloy 825	750	Titanium Diboride	250
Incoloy 657	750	Hastelloy B2	250
Tungsten-Plate	750	Stainless Steel (SS316)	250
Tungsten (PSS)	500	Alonized SS316	250
Tantalum (as received)	750	Zirconium 702	250

Although additional literature on the corrosion of these candidate materials is available, data at this high temperature (900C) and high sulfuric acid concentration (<60%) is sparse. Hence a corrosion study was undertaken to expose the more optimal materials (silicon nitride, silicon carbide and alumina) to simulated corrosion environments (900C, 60% steam, 30% sulfuric acid, 10% air) in order to determine their relative life expectancies.

To accomplish this environmental testing, an exposure loop was setup consisting of a long quartz tube partially housed inside a split tube furnace. The long quartz tube itself holds three large quartz cups and three small quartz cups as displayed in Figure 3. Starting at the top is a large quartz cup filled with quartz chips which acts as an evaporator and gas preheater. Below the evaporator cup sit the three small cups that hold the samples. Below the three sample cups are two large condenser cups, the top of which is filled with Zirconia media and the bottom with SiC media. The long quartz tube is capped on top by a solid Teflon manifold with a pliable Teflon gasket to trap the sulfuric acid vapor and decomposition products in the tube. This manifold is fitted with gas (air/oxygen) feed and a liquid (sulfuric acid) feed. In addition, the condensate is collected and disposed in an appropriate waste barrel.

Figure 3. Sulfuric Acid Exposure Rig.

Once the test setup was completed, ASTM Standard C1161-02C bend bars were scribed, weighed and randomly positioned within three small sample cups. These sample cups were then loaded into the quartz tube and the furnace was heated up to 900°C with flowing argon gas. Once at temperature, the simulated sulfuric acid environment was attained by switching over to air from argon and by dripping in the acid solution. At predetermined intervals (100, 200, 500 and 1000 hours), samples were removed, weighed and fractured according to ASTM Standard C1161-02C procedures.

The results from these studies are found in Figure 4 indicating that the weight gains and mechanical strength for these ceramic materials showed no degradation. Using SEM analyses, it was discovered that through the exposure, a passive silica layer formed on the silicon-based ceramics. This phenomenon is consistent with the apparent strengthening of the materials and their slight weight gains.

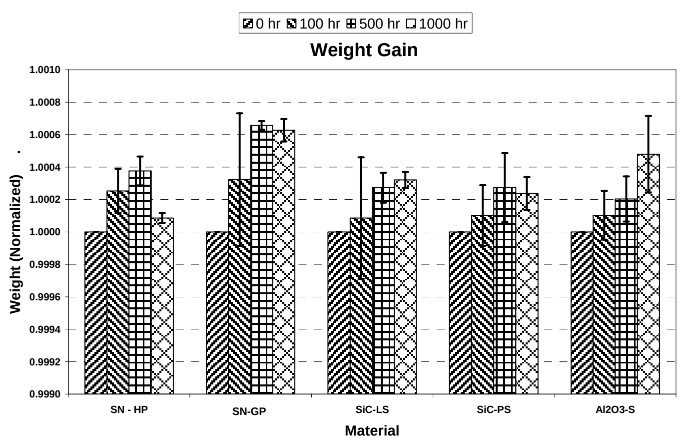

Figure 4a. Weight Gains for 1000 hr Exposure Samples

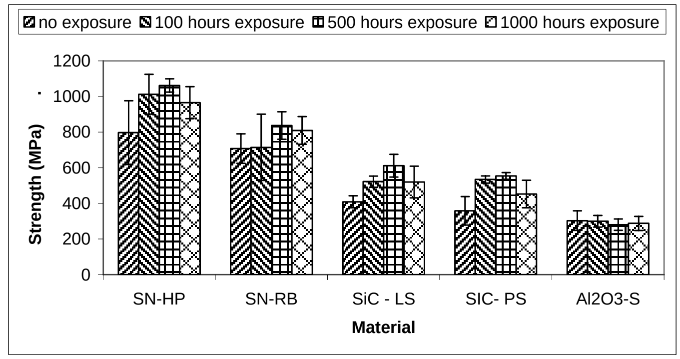

Figure 4b. Strength Change for 1000 hr Exposure Samples

ENGINEERING MODELS

During the operation of this decomposer, the heat exchanger plates are primarily exposed to slight pressure gradients and thermal gradients that can induce stress and promote failure. However in order to capture the extreme conditions during a process trip, the full potential pressure gradient (70 bar) and an extreme thermal gradient (ΔT = 25C inside to out) were imposed stress models. Based on these boundary conditions and loads (Figure 5), the thermo-mechanical stresses were computed for the common repeat unit (micro-channel) within the plate.

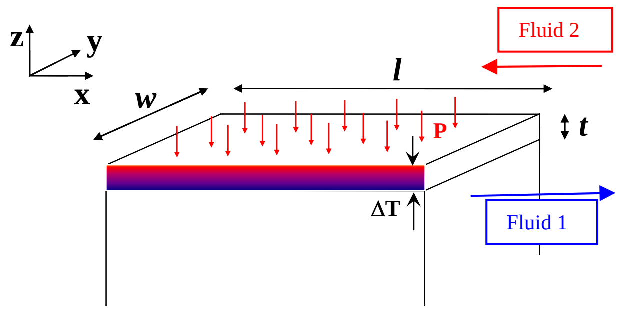

Figure 5. Loading Conditions for Thermo-Mechanical Stresses in Heat Exchanger Plate

Unlike ductile metal components, the reliability of ceramics is dependent of the distribution of stresses and the distribution of flaws within the body. The probability of failure is computed by integrating the stresses and the statistical flaw populations.

Parametric studies investigated the sensitivity of the design geometry (channel width and heat transfer membrane thickness), operating conditions (temperature and pressure) and mechanical properties (characteristic strength and weibull modulus) on the predicted reliability (see Figure 6). By comparing the magnitudes of the probability of failure, one can assess sensitivity of these parameters and calculate a safety factor for any given conditions. The horizontal line indicates the design limit for the probability of failure ($4.2\text{x}10^{-8}$). The central point indicates the baseline design conditions ($1\text{x}10^{-9}$). An increase in most any of the parametric variables results in an improved or reduced probability of failure. The micro-channel width and the operating thermal gradient have reversed trends which increase stress and increase probability of failure – as expected.

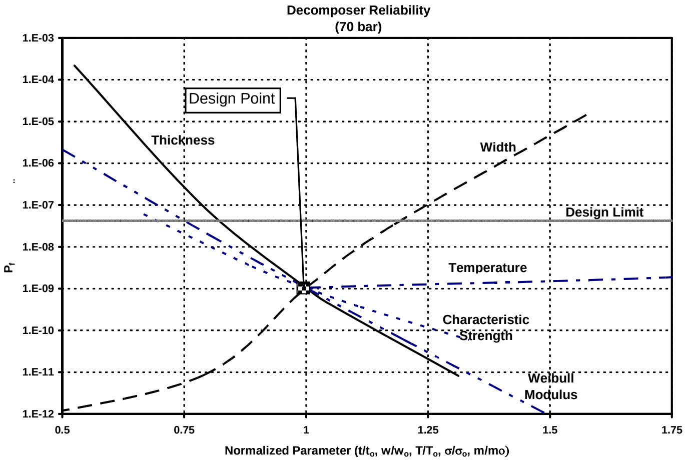

Figure 6. Probability of Failure for Heat Exchanger Plate

One of the primary concerns for the heat exchanger plate is the maldistribution of flow. Imbalanced flow could significantly impact the effectiveness of the heat exchanger plate. Through conjugate flow and heat transfer models (computational fluid dynamics - CFD), performance sensitivity was assessed with respect to these manifold geometries. The initial internal manifold concepts were simple channels scaled to provide sufficient flow with a minimal pressure drop. When modeled, the channels that aligned with the feed headers had excess flows, while those micro-channels that were remote from the headers had significantly reduced or even reverse flows. Figure 7a illustrates pressure field overlaid on the geometry and the respective velocity profiles of the respective micro-channels. These models were used to optimize the plate design by allowing cross communication between channels and by modifying the feed locations as seen in Figure 7b.

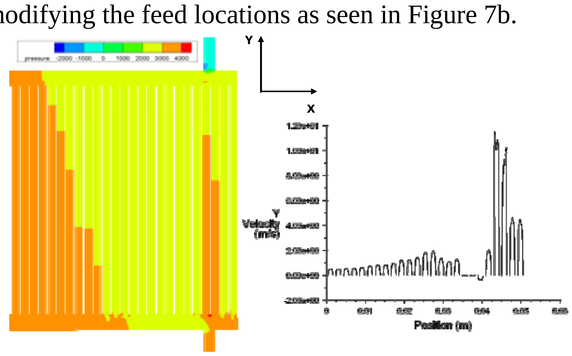

Figure 7a. Conceptual Manifold and its Associated Flow Maldistribution

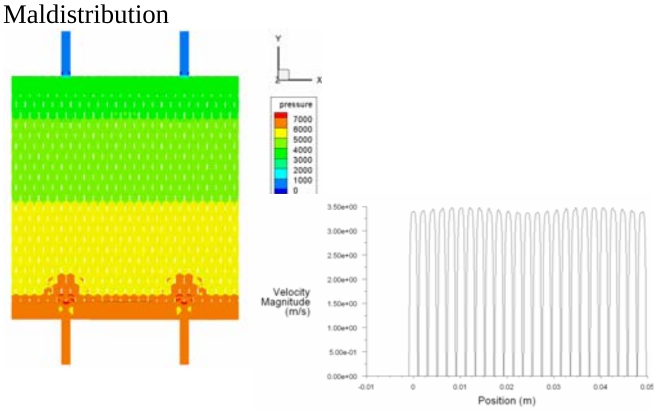

Figure 7b. Optimized Plate Design and its Associated Flow Distribution

DESIGN FOR MANUFACTURING

The Laminated Object Manufacturing (LOM) method is a simple 4 step process. The first process creates a highly plastic, ceramic filled film through a commonly practiced process called tape casting. Second, these films are machined (CNC LASER cutters) into specified patterns which define internal flow channels. Third, these layers/films are laminated together such that interconnecting channels of various layers form the internal flow network. Lastly, these green bodies (unfired, ceramic filled plastic bodies) are densified through thermal processing called sintering. This methodology easily allows for design changes yet is capable of being scaled to commercial production.

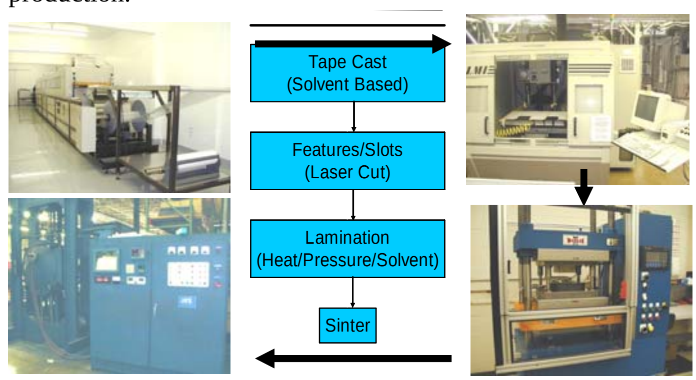

Figure 8. LOM Method for Ceramic Planar Structures

Using the LOM methodology several test coupons with varying channel dimensions (width and depth) were constructed (Figure 9). These sample coupons were used to assess the quality of the internal features and for flow testing.

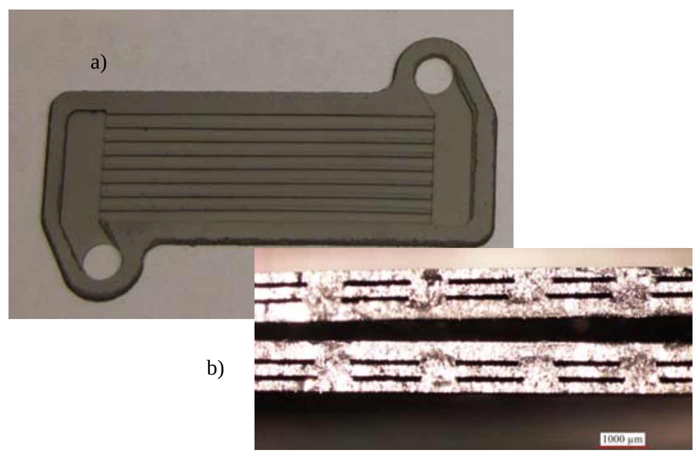

Figure 9. Sub-scale Heat Exchanger Plates – a) Uncapped Plan view [Channels (LxWxD): 45mm x 1250µ x 250µ.], b) Fractured Cross-Section of 2 Plates.

EXPERIMENTAL VALIDATION

Using the as-fabricated test coupons with varying channel dimensions flow tests were performed. By using open-faced structures, Plexiglas cover plates were used that included an array of pressure taps. Using these ceramic flow channels and cover plates the pressure field could be measured at various flow rates and channel dimensions.

The results of these experiments were compared to the computational fluid dynamics models. It was found that the average variation between experimental data and analysis was about 5% (pressure basis). These favorable results lend confidence to these models and their ability to be used in optimizing internal manifolds and channel geometries.

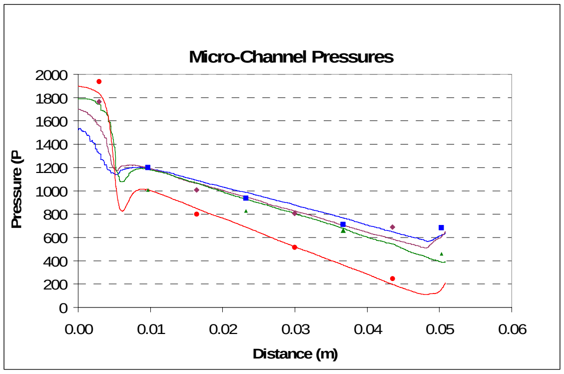

Figure 10. A Comparison: CFD vs Experimental Results.

SUMMARY

It was found that a "shell and plate" design for a microchannel heat exchanger could be applied to sulfuric acid decomposition in the SI process. Corrosion studies indicated that several materials of construction would be feasible under the high temperature, corrosive environments expected. Based on the mechanical properties and the stress models, the reliability predictions are well within the design limits. By analyzing several as-fabricated coupons, it has been demonstrated that the design features (microchannel width and depth) can be achieved by the scalable Laminated Object Manufacturing (LOM) methodology. Flow testing of these coupons also indicates that the as-fabricated channels meet the flow performance (mass flow vs. pressure drop) as needed for this application.

It is presumed that the next steps in developing this high temperature heat exchanger will require component scale-up and thermal operational testing. Scaling of these coupons requires the integration of more channels into a single plate and the joining of multiple plates into a stack. The thermal testing will likely occur in multiple stages where dynamically and thermally similar fluids can be used on well instrumented tests. Subsequent tests would incorporate actual temperatures and process fluids.

ACKNOWLEDGMENTS

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