Ceramic Reactor for Use with Corrosive Supercritical Fluids

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This article describes the development of an alumina reactor used for oxidation in supercritical seawater or other corrosive salt solutions. Normal metal or coated reactors cannot withstand these corrosive conditions, and no constructions are known in the literature to solve the mechanical problems when using ceramics. The corrosion resistance of the alumina tube in this very severe environment is also unknown, but was expected to be sufficient. Therefore, a high-pressure alumina reactor will expand the range of possible experimental conditions and media in supercritical fluid research.

Oxidation of organic substances in supercritical water is used in toxic waste treatment. The treatment of many waste streams demands the complete oxidation of very stable toxic chemicals in the water phase. A wide variety of compounds and waste types, including halogenated ones such as chlorophenols has been oxidized to completion at temperatures around 500°C and pressures around 27 Mpa. An overview of supercritical oxidations has been given by Gloyna and Li (1993) and a general review of supercritical reactions has been given by Savage et al. (1995).

The application we had in mind was to develop an analytical method for the determination of the isotopic ratios and ^{14}C age of dissolved organic carbon (DOC) in seawater (le Clercq et al., 1996). DOC is defined as all organic substances in seawater that pass a 0.2-μm filter. Typical concentrations are 1 mg/L. The central step in the quantitative measurement of DOC is the complete oxidation of these humic-like acids. In our method, oxidation is performed under supercritical conditions and thus the main problem arising is the construction of a suitable reactor.

Oxidizing salt solutions are of a most corrosive nature. Even materials such as Haynes Alloy, titanium, or enamel coatings fail at elevated temperatures. If the reactor survives corrosion, the corrosion process itself can still trouble experiments by the uncontrolled catalytic effect of released metal ions (Yang and Eckert, 1988). In our situation traces of released carbon from corroding alloys would be highly disturbing.

Furthermore, the salts cause an increase in critical pressure. A typical seawater concentration of 3.5% sodium chloride causes the critical pressure to increase by 10 Mpa from 22 MPa for pure water to 32 MPa. The critical temperature is raised only slightly, from 374 to 410°C. A further increase in salt content rapidly increases the critical pressure and temperature (Sourirajan and Kennedy, 1962).

The two main problems in constructing a reactor suitable for these conditions were the construction of a detachable connection to the stainless steel tubing and the insufficient mechanical strength of the alumina. An overview of the system is shown in Figure 1. A high-pressure liquid chromatography pump pumps the seawater into a stainless steel clamp at a pressure of 35 MPa. This clamp is connected to an inconel 800HT tube. Within this tube, an alumina tube has been placed that is sealed by a 90° Sh viton O-ring. A detail of this clamp construction that is fixed by six springs is shown in Figure 2. The springs can exert a force of 500 N each.

An equal amount of distilled water flows at an equal pressure countercurrently around the alumina tube. This minimizes the mechanical stress on the ceramic. It also functions as a heat exchanger, so the seawater is cooled down to room temperature before it reaches the end of the tube.

It is crucial that there is as little space as possible between the steel of the clamp and of the tube (less than 0.1 mm), and some space between the alumina and the clamp (more than 0.2 mm); otherwise, a very slight deformation of the outer tube leads to stress on the alumina and to breakage of the inner tube.

The pressure of both flows is reduced by leading the fluids

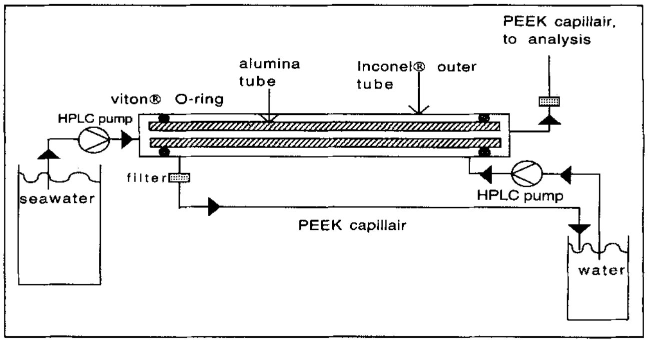

Figure 1. Supercritical oxidation apparatus.

The oven used to heat the reactor has been omitted for the sake of clarity.

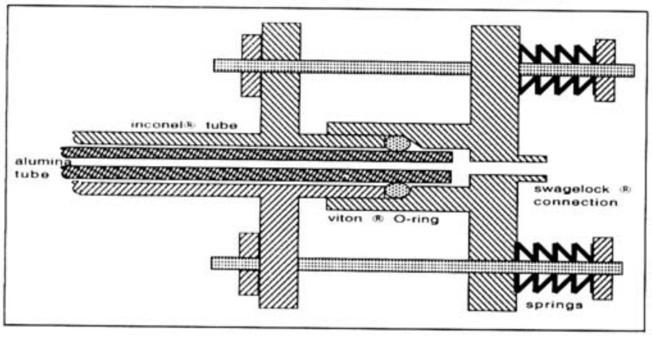

Figure 2. O-ring sealing of the alumina tube.

through a length of 0.13-mm-ID polyethertetherketone (PEEK) tubing. A 0.5-μm filter has been placed in front of this capillary to prevent particles from clogging it. In order to change flow and pressure independently, the length of the tubing has to be changed. This is a slight drawback of this pressure reduction method. A 50-cm section in the middle of the reactor is heated. In the development of the reactor several aspects appeared to be crucial. Originally, no counterpressure was applied and the two clamps were connected by six bars that remained at room temperature. Several types and sizes of alumina tube were tested with this setup, but all failed at conditions below the desired ones. The largest tube tested had an ID of 2 mm and an OD of 15 mm, and even this tube exploded at 31 MPa and 400°C. The strength of the alumina is around 100 to 500 MPa and does not decrease significantly with a raise in temperature to 800°C (Dörre and Hübner, 1984). This indicates that the failure of the tubes cannot be explained by insufficient strength across the tube, but by the occurrence of a buckle. This was confirmed by the rather improved performance of the next version. Instead of six bars, the clamps were connected by a stainless steel tube that was heated together with the alumina within the oven. The thermal expansion coefficient of stainless steel and higher nickel alloys such as Inconel is larger than that of alumina (16 and 8×10^{-6} K^{-1}, respectively) so there is no danger of buckle during heating in this construction. An alumina tube with an OD of 8 mm and ID of 4 mm endured a pressure of 30 MPa of salt solution and a temperature of 600°C, but failed after 26 hours at these conditions. As alumina does not show fatigue or creep, and corrosion was the most plausible cause.

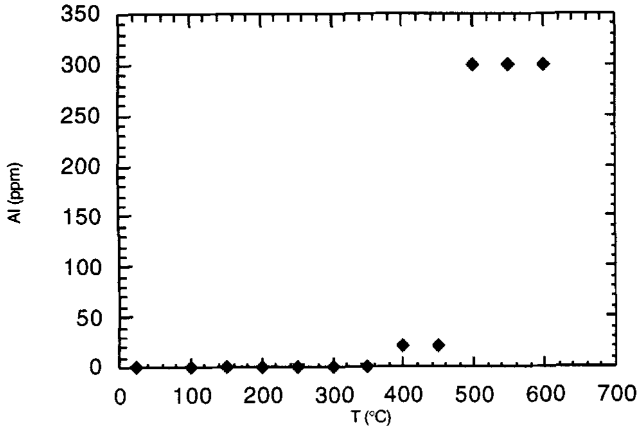

Figure 3. Elutriating alumina of the tube without applying a counterpressure.

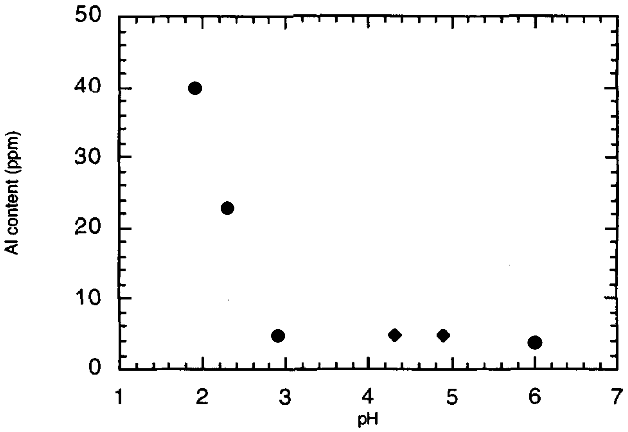

Figure 4. Influence of the pH on corrosion of the alumina tube at 500°C, applying a counterpressure.

Corrosion was therefore monitored by determining the aluminum content of the eluent. A mixture of 35-g NaCl and 1-g Na_2CrO_4 in a liter of water was led through the reactor at a pressure of 34 MPa, and a varying temperature at a rate of 1 mL per minute. The results are given in Figure 3. Below 350°C no corrosion can be measured; above this temperature it is rapid (300 ppm aluminum equals a rate of 1 μm/h). The constant values above 450°C may be due to a limited solubility of alumina in these conditions and could give a wrong view of corrosion.

The counterpressure in the final version prevents the mechanical strain in the alumina that in our previous version led to stress induced corrosion and a rapid failure. The same experiment with a counterpressure gave no alumina up to 700°C. With seawater, a trace was found around 0.3 ppm.

Because the pH may vary in our application, its effect on the corrosion was tested and results are shown in Figure 4. It shows that it has no effect on corrosion as long as the pH remains above 3, and causes a tenfold increase with a pH decrease to 2.

We have constructed an alumina reactor that can be used with acidified salt solutions at supercritical conditions. It is superior in corrosion resistance to the conventional nickel alloy or titanium ones, and may be of interest to chemists in other disciplines. The overall resistance to corrosion of this reactor is sufficient for our purpose. Application of it in catalysis research would make experiments at truly low levels of metal concentration possible. It can also be used for material research in severe environments.

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