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January 10, 1994

Dr. Hussain Al-Ekabi
Hitech Advanced Photo-Oxidation Inc.
71 Brandy Lane Rd.
London, Ontario, Canada N6G 4S2

Dear Dr. Al-Ekabi:

As we discussed in our telephone conversation last month, I am pleased to extend my abstract on "Corrosion and Salt Deposition Issues in a Supercritical Water Oxidation Reactor" for The First International Conference on Advanced Oxidation Technologies for Water and Air Remediation.

This paper, by Steve Rice and myself, will deal primarily with engineering issues associated with designing and building a reliable reactor. We have an extensive engineering program with three functioning reactors to meet different needs at Sandia, and are in the process of designing a larger one to be located at McAlester Army Ammunition Plant in Oklahoma. Central to building a successful SCWO waste processing system are the issues of salt deposition and reactor corrosion which this paper addresses. We believe that it would prove valuable and interesting to your intended audience.

Steve Rice will be submitting an abstract on modeling and experimental studies on the oxidation chemistry of simple molecules for the paper you and he discussed in September. It will be of a separate and distinct nature. The call for papers in the second circular on the conference indicates that the submission of additional abstracts for papers is appropriate, and, as a result, we would like to submit more than one abstract for presentation in the parallel sessions.

I will call you in a couple of weeks to verify receipt of the enclosed material. Thank you for consideration.

Sincerely

Costanzo A. LaJeunesse

cc:
S. F. Rice - 8361
H. H. Hirano - 8412
M. C. Stoddard - 8412

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Corrosion and Salt Deposition Issues in a Supercritical Water Oxidation Reactor

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Abstract

Supercritical water oxidation (SCWO) is an emerging new method for destroying aqueous organic waste. SCWO is conducted at temperatures and pressures above the critical point of water (374°C, 22.1 MPa) where water can exist in a single phase with most organic chemicals as well as gases such as oxygen, CO, and CO₂. Depending on residence time, feed concentration, and temperature, this single phase reaction environment will rapidly produce innocuous combustion products from a wide variety of industrial wastes.

However, oxidation of organic material containing heteroatoms, such as sulfur or phosphorous, will form acid anions. In the presence of metal ions, salts are formed which precipitate out of the supercritical fluid. These salts deposit in the reactor and affect the processing of organic material. The oxidizing process in the presence of acid anions appears to corrode the reactor, with dissolved heavy metals appearing in the effluent.

A robust waste processing system must accommodate the formation of these salts and avoid reactor corrosion. To design such a system, it is important to understand the deposition and corrosion process quantitatively. This paper is a report on an experimental program to understand the salt deposition and corrosion phenomena in a tubular inconel 625 reactor from the processing of water soluble dyes. Destruction and removal efficiencies (DREs) for 10 seconds of residence time for the destruction of a colored dye are also reported.

Reactor Configuration

All tests were performed in one of Sandia's supercritical water oxidation tubular reactors. This reactor is approximately 750 cm long, with two 90° turns at 260 cm and 300 cm. Thermocouples are located in the flow approximately every 60 cm at T-unions joining individual sections of 1.42 cm (9/16 in) O. D. - 0.47 cm (3/16 in) I. D. inconel 625 tubing. The first 260 cm of the reactor is equipped with heaters capable of adding power at a rate of 17 watts/cm; the second section is powered at a rate of 5.4 watts/cm and is designed to maintain isothermal conditions over a length of 490 cm. Pressure transducers and thermocouples immersed in the supercritical fluid are placed at locations throughout. The readings of these transducers and thermocouples are recorded continuously throughout a test such that the development of a plug or constriction can be detected as a pressure differential from one transducer to the next.

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Operational Methods (salt studies)

An initial temperature of 325-330°C (fluid temperature) in the isothermal section of the reactor is established with distilled water. A 0.5 wt% solution of Na₂SO₄ or NaCl is then introduced with the same flowrate, as the pure water is simultaneously decreased. Concentration in the effluent is measured by a Na⁺ specific ion electrode. The temperature is progressively increased yielding a curve of salt concentration in the effluent versus temperature. Figure 1 shows the results at 250 and 500 bar for Na₂SO₄.

Operational Methods (corrosion studies)

A temperature profile is established with distilled water. H₂O₂ at concentrations between 1.5 and 12 wt% is introduced into the reactor along with a 0.25 - 2.0 wt% Amido Naphthol Red G dye (C₁₈H₁₃N₃O₈S₂Na₂) solution. The effluent is monitored for Na, Cr, Ni, and Mo ion concentration, pH, and total organic carbon (TOC). The TOC results are converted to a destruction efficiency based on TOC in the feed.

Results and Discussion

The destruction of Amido Naphthol Red G dye results in the formation of Na₂SO₄. During the destruction of the dye, pressure increases before the portion of the reactor having a fluid temperature between 300-400°C and subsequent examination of this reactor section shows that a solid plug of Na₂SO₄ is formed. Destruction of the dye forms Na₂SO₄ which precipitates onto the reactor walls until the flow path is constricted. Figure 1 shows that the amount of Na₂SO₄ transported through the reactor decreases exponentially with temperature and is only marginally increased by a doubling of pressure. This is consistent with work by Armellini and Tester (*J. Supercrit. Fluids*, 1991, 4, 254) on the phase diagram of Na₂SO₄ in water at supercritical pressures and temperatures. At 360°C, 0.5 wt% of salt can coexist in a single phase in water; any excess must precipitate out as a solid. As temperature increases, the solubility rapidly approaches zero.

The results from a representative corrosion test is presented in Table 1. Note that in Test 1 some metal contamination is evident. Cr concentration can be reduced to nondetectable levels if pure water is run for about 8 hours. The nominal residence time at temperature was 10 seconds. All the dye is completely destroyed over the range of experimental conditions reported (> 99.4 % DRE).

The corrosion effects affiliated with the oxidation of the dye are complicated and are connected to the composition of the feed. Of particular interest is the metal selectively exhibited whether or not the feed dye is present. Chromium is selectively leached by excess oxygen. When only H₂O₂ is flowing in the reactor (tests 2, 6, 7) the Cr concentration in the effluent is 2.1 to 5.1 ppm. It is reduced by an order of magnitude when the dye is introduced (tests 3, 4, 5, 8, 9) and the oxygen is consumed. Conversely, nickel and molybdenum are selectively leached by the presence of the dye in the feed. Ni and Mo are not detectable in

the effluent when pure water or water with H₂O₂ are input, but rise to a concentration of 38 when 2.0 wt% dye is introduced. Based on the results of tests 8 and 9, the amount of Ni and Mo leached is only dependent on initial dye concentration (it is probably dependent on acidity). It is not dependent on excess oxidant concentration because almost all the oxygen is consumed in test 8 and the amount of Ni and Mo leached is nearly the same as test 9 where an equivalence ratio of two is used.

Figure 1: Plot of salt concentration in the reactor effluent as a function of system pressure and reactor temperature for Na₂SO₄ feed at 0.5 wt%.

Table 1. Effluent Analysis.

Test #	Dye (wt %)	H ₂ O ₂ (wt%)	T (°C)	pH	Na (ppm)	Cr (ppm)	Ni (ppm)	Mo (ppm)	DRE
1	0.0	0.0	500	7.09	0.20	0.17	nd	nd	n m
2	0.0	1.5	500	4.93	0.50	2.10	nd	0.1	n m
3	0.25	1.5	500	2.88	7.63	0.10	4.7	0.75	99.4
4	0.25	1.5	550	2.68	1.15	0.14	3.85	0.60	99.6
5	0.25	1.5	580	2.68	1.25	0.19	2.98	0.64	99.4
6	0.0	6.0	550	4.14	2.08	5.1	nd	nd	n m
7	0.0	12.0	550	4.27	nd	3.9	nd	nd	n m
8	2.0	6.0	550	1.97	53.2	0.09	38.0	1.90	99.9
9	2.0	12.0	550	1.95	70.0	0.78	35.0	2.15	99.8

nd=not detectable

nm=not measured

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