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Concentrated Hydrogen Peroxide**

R. Boxwell, G. Bromley, D. Mason,  
D. Crockett, L. Martinez

Orbital Sciences Corporation,  
Launch Services Group

Chandler, AZ

C. McNeal

NASA Marshall Space Flight Center, AL

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# MATERIALS COMPATIBILITY TESTING IN CONCENTRATED HYDROGEN PEROXIDE

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Orbital Sciences Corporation  
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## ABSTRACT

Material test methods from the 1960's have been used as a starting point in evaluating materials compatible with high concentration hydrogen peroxide for use in today's space launch vehicles. These established test methods have been modified to incorporate today's analytical laboratory equipment and to test a wide range of materials to incorporate the revolution in polymer and composite materials that has occurred since the 1960's. Testing is accomplished in 3 stages from rough screening to detailed analytical tests. Several interesting test observations have been made during this testing and are included in the paper. A summary of the set-up, test and evaluation of long-term storage sub-scale tanks is also included. This sub-scale tank test lasted for a 7-month duration prior to being stopped due to a polar boss material breakdown. Chemical evaluations of the hydrogen peroxide and residue left on the polar boss surface identify the material breakdown quite clearly. The paper concludes with recommendations for future testing and a specific effort underway within the industry to standardize the test methods used in evaluating materials.

### 1. Introduction

Test methodologies from the 1960's to determine a materials compatibility in a concentrated hydrogen peroxide environment have been investigated and modified for use in modern day rockets and space launch vehicles. A modified series of tests were developed to provide useful information to the design engineer of new hydrogen peroxide systems. This new approach has been in-test for the last two years. This paper summarizes the test approach, the materials tested, lessons learned and future test recommendations.

### 2. Test Methodologies

A significant amount of materials testing in concentrated hydrogen peroxide was performed during the 1950's and 1960's. Much of this data is used as a starting point in materials selection and is published

in FMC, Shell, and Solvay documents. These documents classify materials in four Classes based on their ability to be used in hydrogen peroxide systems. Class 1 is the best and preferred class for long term storage. Classes 2 and 3 offer limited hydrogen peroxide system exposure and Class 4 is reserved for materials that should not be used for hydrogen peroxide contact.

Our interest today is to build upon this baseline of test data and offer design engineers a listing of materials available for current and future hydrogen peroxide systems. In doing so, we have modified some of the test approaches to utilize modern laboratory technology that in many cases offer more sensitive results that can be directly applied to the design process. We are also updating the baseline list of materials to incorporate the tremendous revolution in polymer and composites technology that has occurred since the 1960's.

Table 1 outlines the major test methods used both in the 1960's and today at Orbital:

The key objectives for materials compatibility are:

- a. Ensure that the hydrogen peroxide does not degrade the candidate materials through swelling, weight change, visible cracking, crazing, chipping, discoloration, disintegration or mechanical property loss.
- b. Quantify each candidate materials chemical element or compound contamination in hydrogen peroxide that could harm the peroxide concentration stability.
- c. Verify that the material/peroxide combination does not react to form explosive by-products.
- d. Evaluate each materials contamination to hydrogen peroxide with the intended catalyst bed performance.

These tests, evaluations and verifications are made

**TABLE 1. MAJOR TEST METHODS**

Test Method	1960's Use	Recommended Use	Data Provided
Active Oxygen Loss (AOL)	X		Quantitative/qualitative decomposition rate of peroxide
Hydrogen peroxide stability	X	X	Stability of the hydrogen peroxide after a specific exposure
Visual observation	X	X	Detects physical degradation mechanisms such a crazing, cracks or dissolution
Materials weight change		X	Quantitative determination of peroxide intake and material loss
Materials volume change		X	Quantitative determination of material swelling
Hydrogen peroxide analysis after test		X	Quantitatively determines trace elements and impurities transferred into test peroxide after exposure to a specific material
Impact sensitivity	X	X	'Go/no-go' test for synergistic detonation due to impact
Mechanical property loss		X	Quantify material property knockdowns due to hydrogen peroxide exposure

through a series of beaker soak tests, quantitative chemical analyses, drop weight impacts and mechanical testing. The test outline for materials in concentrated hydrogen peroxide is as follows:

Stage 1 is a rough screening process to eliminate obvious noncompatible materials. Tests include exposure to room temperature and 142 °F hydrogen peroxide by limited immersions to screen out incompatible materials.

Stage 2 determines the materials compatibility with concentrated hydrogen peroxide. Tests include a hydrogen peroxide stability determination after exposure to the test material, the materials surface texture, appearance changes, swelling, weight change and mechanical strength loss after exposure.

Stage 3 is where an analytical evaluation is made to quantify the hydrogen peroxide degradation and contamination change after exposure to the subject test material. Tests are used to determine the type and quantity of contamination in the hydrogen peroxide by Ion Chromatography (IC), Inductively Coupled Plasma (ICP/MS), and Total Organic Carbon (TOC). Impact sensitivity of the test material after exposure to hydrogen peroxide is also contained at this stage.

**3. Summary of Materials Tested and Interesting Findings**

Initial testing to identify peroxide compatible materials followed a shotgun approach. Numerous materials supplied by different resin and composite manufacturers were tested in the hopes of finding a system that offers improved performance. These tests followed the 3 staged approach previously described. The results of these tests are:

- a. Stage 1 testing started at 86 different metals, resins, fibers and/or composite laminate materials and yielded 46 for future evaluation in phase 2.
- b. Stage 2 testing started with 46 materials and yielded 12 for full stage 3 evaluation to date.
- c. Stage 3 testing is still in-progress and is focused on testing 8 specific material types. These materials include epoxy resins, fluoropolymers, specific stainless steels, and metal coating systems.

There are several items discovered through these series of tests that are interesting to note and/or will require consideration in future designs. These items are:

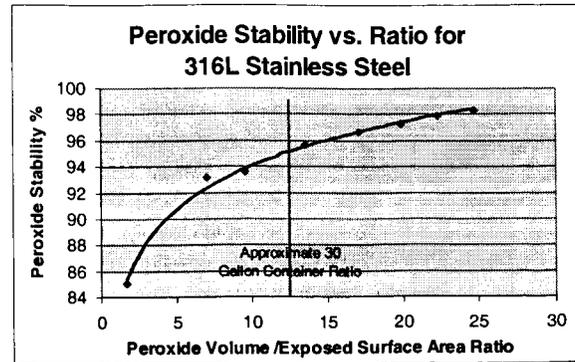
- a. We continue to run into a temperature 'wall'

when accelerating exposure tests. In a series of Arrhenius tests to calculate the activation energy and rate constant for specific materials, we found an elbow in our plotted data near certain temperatures. For the non-metallic materials we tested it was in the area of 155-160 °F and around 190 °F for metals. We since keep our accelerated test temperature at 142 °F so not to experience this phenomena.

- b. We can use the general rule that the chemical reactions in peroxide approximately double for each 10 °C temperature increase to predict accelerated exposure times for elevated temperature compatibility tests. A 1 year accelerated exposure can be performed in 14 days at 142 °F.
- c. Fibers for composite systems have amazing compatibility with peroxide. We tested T-1000, T-650, AS4, Kevlar and two E-Glass weaves. Kevlar was the only material that showed visible degradation from the exposure. Fiber sizing is still to be addressed.
- d. Materials degrade by six primary mechanisms; dissolution, bleaching, surface crazing & cracking, weight or volume change, internal swelling & cracking and by an outer crust formation.
- e. Test quantities of peroxide as compared to exposed surface area of the material in question do influence resulting concentration values. The curve shown in Figure 1 was derived from stainless steel 316L tests, but is believed to show a generic trend in peroxide volume to exposed surface area of a test material. This trend is very important when comparing test data from one material to another.
- f. It appears to us that surface finish will result in a similar trend as that shown for the peroxide to surface area ratio. We only have rough observational data, but samples with rougher surface finishes usually result in lower peroxide concentration stabilities

#### 4. Sub-Scale Tank Long Term Storage Test Results

We attempted to contain 85% hydrogen peroxide in the sub-scale tank for the duration of 1 year with minimal affect on the peroxide concentration stability. This test period was ended after 34 weeks due to an accelerated decomposition of the peroxide. The tank was drained and its components



**Figure 1. Hydrogen Peroxide Stability verses Ratio**

examined in order to determine the cause of the sudden acceleration in peroxide degradation.

Starting at 30 weeks we noticed a trend in the weekly concentration of the sample taken from the tank. Increased observation of concentration, tank temperature and tank venting were incorporated as well as increased peroxide sample collection. At 34 weeks the tank temperature had risen to 10 °F above ambient and the experiment was ended. A small amount of hydrogen peroxide was saved for outside analysis.

The initial test plan for monitoring the sub-scale tank progress included a weekly reading of the peroxide concentration and a quarterly analytical evaluation of hydrogen peroxide chemical changes from a local outside lab. This final analysis of the subscale tank incorporates data from several sources including:

- a. The weekly refractive index (RI) readings that we made each Friday of the 34 week exposure
- b. The hydrogen peroxide chemical analysis results from the original supply lot, from the sub-scale tank at 3 months, at 6 months and at 2 intervals during the decomposition phase. Chemical analysis includes Ion Chromatography (IC) to detect sodium, ammonium, potassium, magnesium, calcium, chloride, bromide, nitrate, phosphate and sulfate; Total Organic Carbon (TOC); and Inductively Coupled Plasma (ICP) to detect for metal elements including Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, P, Se, Si, Ag, Na, Sr, Ti, Sn, Ti, V, and Zn.

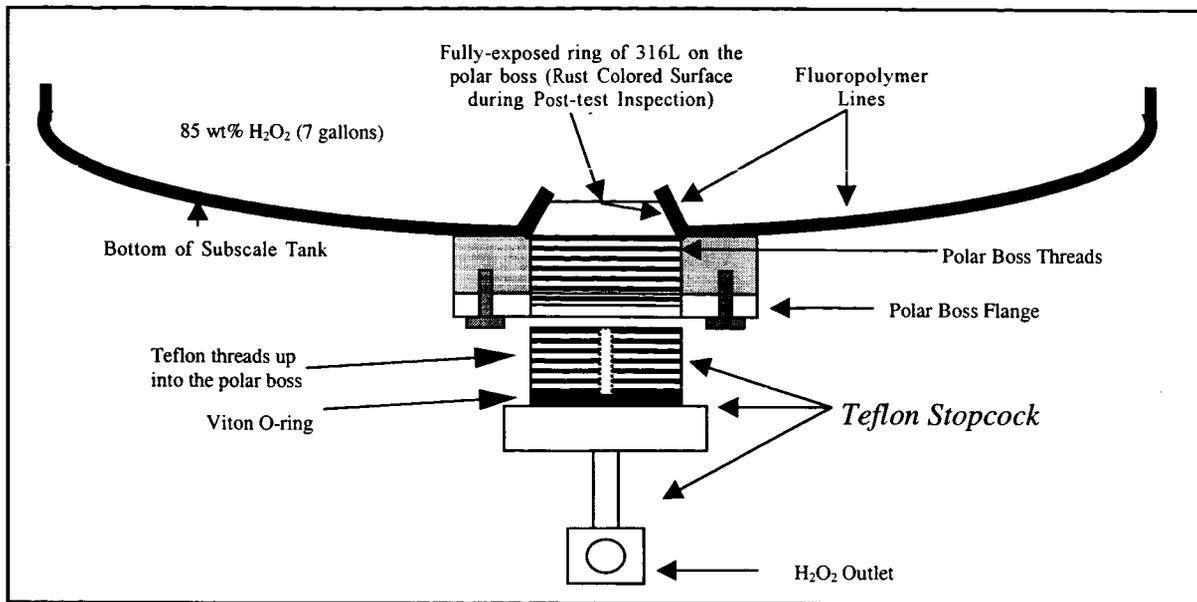


Figure 2. Sub-Scale Tank Lower Section Layout

- c. Visual examination of the sub-scale tank as it was disassembled and drained.

#### 4.1. Background Information

Each material used in the tank was tested separately by performing an accelerated exposure test. The accelerated test consists of soaking the material for 2 weeks in 85%  $H_2O_2$  at 142°F (which is equivalent to a one-year exposure at room temperature) and measuring the concentration of the resulting solution. The hydrogen peroxide is considered stable with materials that yield low changes in concentration. All materials used in the sub-scale tank system were considered to be fully compatible with the peroxide based on the individual results of previous accelerated tests. The bottom end configuration of the sub-scale tank is shown in Figure 2.

#### 4.2. Storage and Test of the Sub-Scale Tank

**Storage Environment.** The tank resides in a lab environment. The temperature variations in the lab range between 20-25 °C in the summer and 25-29 °C in the winter. The room is secured from non-essential personnel but is not a particulate controlled area. The air vent on the tank was made small and covered with aluminum foil to keep contamination out of the tank.

**Weekly Testing.** Each week a 20 ml sample of

hydrogen peroxide was drained using the stop-cock at the bottom of the tank to measure the refractive index of the hydrogen peroxide. The refractive index was then correlated to a concentration and charted as a function of storage time. Figure 3 shows the plot of these tests.

**Quarterly testing.** Each quarter of storage, a 60 ml sample of hydrogen peroxide was captured from the bottom of the tank using the stop-cock and chemically analyzed.

#### 4.3. Test History, Results and Problem Investigation

##### 4.3.1. Test History

The sub-scale tank hydrogen peroxide concentration was monitored once per week until the final week, in which it was monitored every one or two days to ensure that it wasn't decomposing too quickly. Once the decomposition rate increased in the final week to over 5 wt%/week, the ability for the tank to effectively dissipate heat was lost and the temperature started to rise (further accelerating the decomposition).

##### 4.3.2. Tank Visual Examination

Once the hydrogen peroxide was removed, the inside of the tank was visually examined. No visual indications of damage or other abnormalities of the tank liner were observed.

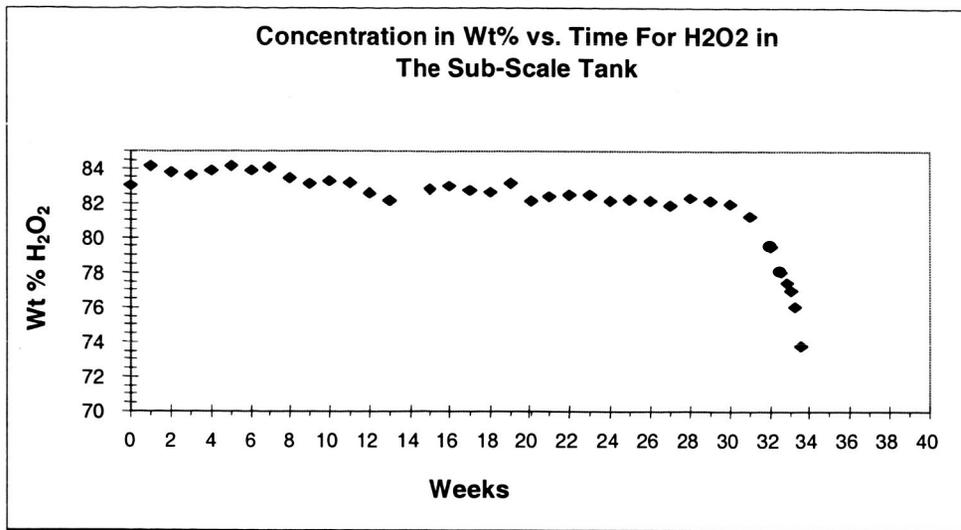


Figure 3. Sub-Scale tank H<sub>2</sub>O<sub>2</sub> Concentration vs. Time

#### 4.3.3. Polar Boss

Exposed surface area of the polar boss to hydrogen peroxide show a light rust colored surface when removed from the tank. This rusty surface appearance continues from the knife edge lip to the last wetted thread on the boss where the Teflon plug is in-place. Figure 4 shows the polar boss after test.

A closer magnified view of this area showed that the rust looking surface appearance is dried out and rolled up at the sides. This discolored material was evaluated using a Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Analysis (EDX) to determine it's chemical makeup. Figures 5 and 6 show these results, respectively.

The material was a Sn/Fe compound. It appears that the Sn used as a stabilizer in the hydrogen peroxide combined with the Fe on the surface of the polar boss, but not with the other alloying elements.

#### 4.3.4. Peroxide Examination

The hydrogen peroxide was poured from the tank into clear beakers and examined. The peroxide was visually clear in color and tint. Throughout the entire 34-week test period of the sub-scale tank, small representative quantities of the tank solution were periodically removed and sent to a local analytical lab for ICP and IC analysis. Figure 7 is a table of the chemical analysis of the sampled

hydrogen peroxide at various times and shows an increase in stainless steel alloying elements as a function of tank storage time.

It is interesting to note the rise in concentration of most of the major alloying elements in the 316 stainless steel in the sub-scale tank peroxide over time (most notably the Cr, but excluding Fe). We believe this suggests a breakdown of the 316L passivation film and scavaging of the Fe by the stabilizer in the hydrogen peroxide.

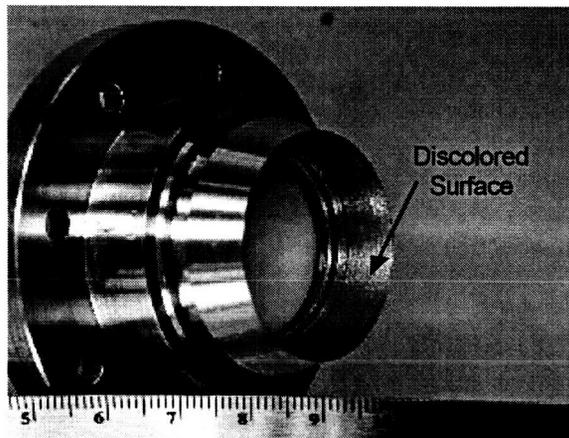


Figure 4. Discolored Polar Boss from Sub-Scale Tank

### 5. Recommendations for Future Testing

The materials compatibility testing performed has been a trial and error learning experience both in individual materials tests and component level tank testing. As a result, the following recommendations for future testing are suggested.

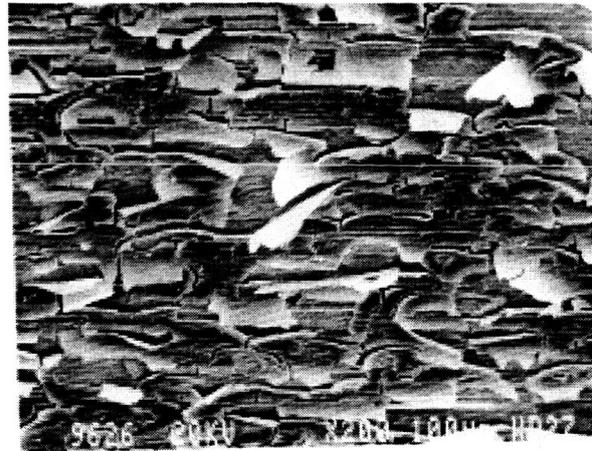
- a. Polar Boss Material Selection – Coat the stainless steel polar bosses with a protective coating or change the material to one more compatible with hydrogen peroxide.
- b. Eliminating internal 'wet' threads in polar boss designs will further reduce peroxide degradation. Design attributes that reduce exposed surface area and eliminate stagnant zones of hydrogen peroxide will be beneficial. These stagnant zones are typically where crevice corrosion type mechanisms form that are detrimental to stainless steel passivity.
- c. Standardize test methodologies for hydrogen peroxide materials testing so they are repeatable and can be generically applied to multiple projects.

### 6. Materials Test Protocol Standardization

A meeting was held in April of 2000 where members of several agencies and aerospace companies gathered to discuss how materials are currently tested in concentrated hydrogen peroxide. The goal of this newly established working group was to begin the process of establishing a set of minimum test methods for use in the aerospace industry and specifically on space structures and satellites. A draft test protocol was the result of this meeting. It is only the beginning step of a long process of standardization that we hope will result in a test method procedure under ASTM or AIAA control.

The basic skeleton of the test protocol was outlined at this meeting. Specific people and/or groups were identified who have volunteered to provide information or actual test method text. Inputs will be gathered, collated and sent back to the group for review.

The test protocol will consist of a series of staged tests to establish a minimum set of data on the compatibility of the subject material in concentrated hydrogen peroxide. Materials that pass this minimum test criteria will then be placed on a list of materials for consideration in future vehicle design applications. It is the responsibility of each new program to use this minimum data set along with



**Figure 5. Higher Magnification of Reaction Compound Flakes Found on the Polar Boss Between Threads**

additional specific test data to ensure that the application is correct and safe.

### 7. Summary

Using 1960's documentation as a starting point, materials compatibility testing in concentrated hydrogen peroxide is being modified and conducted. The 1960's baseline of both test methods and types of materials are being expanded to better suit the needs of today's space launch vehicles. Tests at both the individual material and component tank level have resulted in interesting findings and recommendations for future testing. A standardized materials test protocol for hydrogen peroxide systems in the aerospace industry is strongly encouraged.

### References.

1. 'Bulletin No. 104, Materials of Construction For Equipment in use with Hydrogen Peroxide', FMC Chemicals, 1966 Revision
2. 'Concentrated Hydrogen Peroxide H<sub>2</sub>O<sub>2</sub> Properties, Uses, Storage, Handling', Shell Chemical Company
3. 'Hydrogen Peroxide Rocket Manual', James McCormick, FMC Corporation 1967 Revision

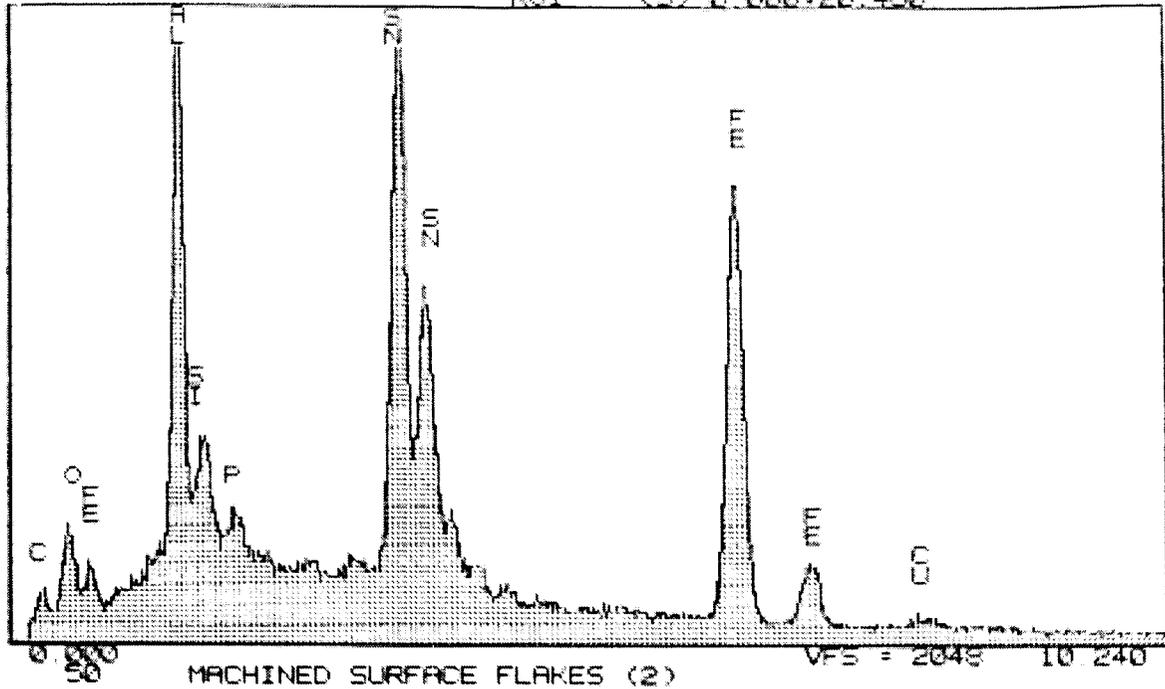


Figure 6. EDX Spectrum of Flakes Removed from Polar Boss. The Tin (Sn) and Iron (Fe) Peaks Are Characteristic of the Flakes. The Aluminum and Copper Peaks Are Due to the Sample Holder Alloy

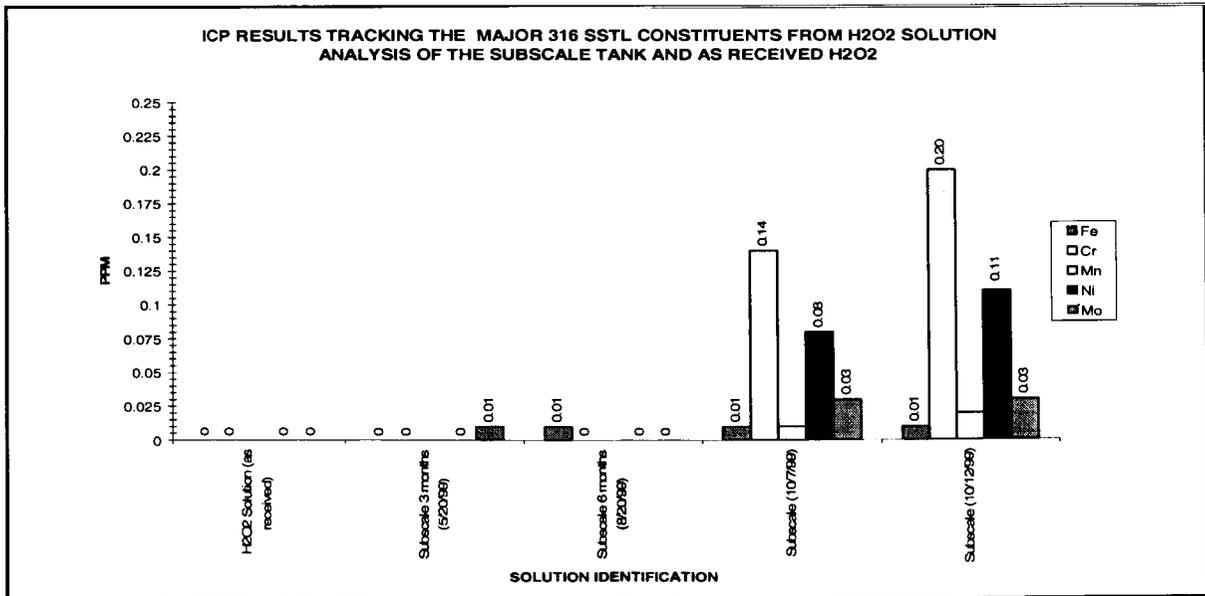


Figure 7. ICP Results Revealing an Overall Increase in Concentration of the Major 316L Stainless Steel Alloying Elements in the Sub-Scale Tank Solution Over Time