

# HAZARD LEVEL OF HYDROCARBON FILMS IN OXYGEN SYSTEMS

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"How clean is clean" is an expression frequently heard when the discussion concerns cleaning an oxygen handling system. Present knowledge of oxygen-fuel systems indicates there is a certain level of contamination that can be safely tolerated. This level will be affected by such factors as type of contaminant, pressure and temperature.

The question: "What is this tolerable limit and exactly what effect do these various factors have?"

Commercial practice is not satisfactory for the systems required for liquid propellant rockets. After an analysis of the degree of cleanliness of successful systems, a level of four milligrams of hydrocarbons per square foot was established. This degree of cleanliness produces acceptable systems—but is costly in both time and money. Often five or six steps of washing, flushing, and purging are required.

## The investigation

Under an Air Force contract, Air Products and Chemicals Research and Development Department has investigated the possibility of ignition of a hydrocarbon film on the wall of piping for oxygen service for the purpose of better defining the safe level of contamination. While this work is not yet complete, the results to date have been informative:

For these tests, n-hexadecane was used as the hydrocarbon contaminant as its boiling temperature and molecular weight are in the range of common lubricants. The experimental equipment consisted of a schedule 40 stainless steel pipe section two feet long, one inch nominal diameter, with a six inch long section of one-half inch stainless steel at each end. For the runs involving gaseous oxygen, rupture discs made from modified one-half inch unions and brass foil were installed on one end of the section.

The hydrocarbon film was applied to the inside surface from a solution of n-hexadecane in carbon tetrachloride which was evaporated in a hot water bath while rotating the pipe section to achieve uniformity of the hydrocarbon film. The quantity of hydrocarbon deposited on the surface was controlled by the quantity and concentration of the feed solution. After application of the film, the pipe section was cooled to room temperature and the igniter and oxygen line connected. After purging the pipe section for five minutes to insure removal of the last traces of the solvent vapors, the rupture disc assembly was tightened, the oxygen pressure raised to the desired setting and ignition applied.

## Blank runs

The pipe assembly was then disassembled and the unburned hexadecane dissolved in two batches of fresh carbon tetrachloride. This solvent was then combined and concentrated by evaporating most of the solvent. After measuring the quantity of the concentrate, the concentration of n-hexadecane was determined by a Beckman IR-4 infrared analyzer. For blank runs the same procedure was followed except ignition was not applied and pressure was held at 50 psig for five minutes.

## Liquid oxygen

For runs involving liquid oxygen the one-half inch end sections were removed after the film was applied and one end of the one inch diameter section capped. Rather than pour the liquid oxygen in, the experimental section was immersed in a vertical position in liquid nitrogen and gaseous oxygen condensed until the section was about 80 per cent full. Following ig-

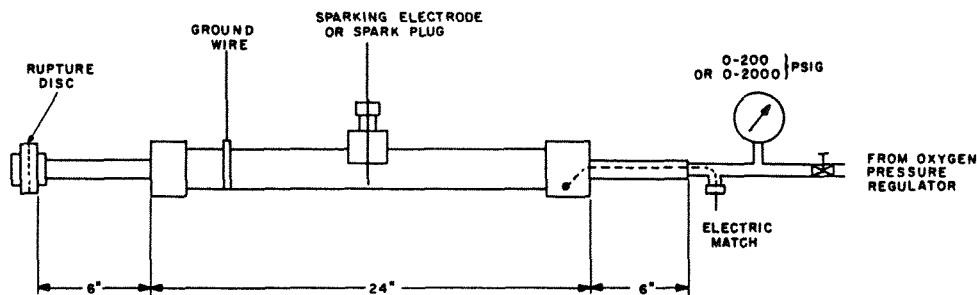


Figure 1. Ignition apparatus using gaseous oxygen.

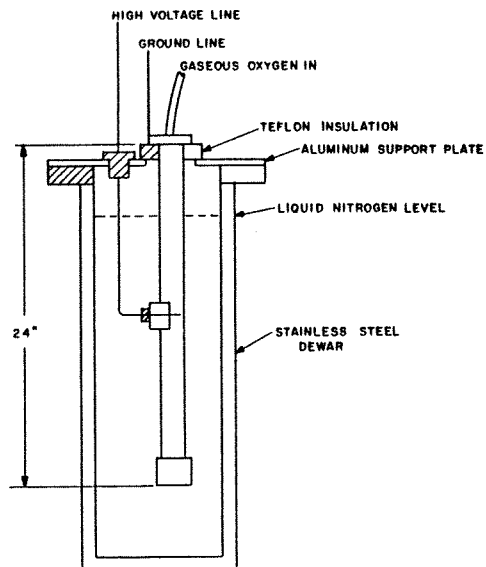


Figure 2. Ignition apparatus using liquid oxygen.

nitron, the pipe was removed, warmed slowly and the same analytical procedure followed as noted previously.

Two forms of ignition were used. The first mechanism was high voltage spark. A Model T Ford ignition coil was used with an electrode made either

from a length of nichrome wire in a compressed Teflon insulator or a copper wire soldered to the tip of a spark plug.

The electrodes were inserted at the middle of the pipe and the tip of the wire maintained at a distance of five mm from the opposite pipe wall which served as the grounding electrode. The power input to the coil was five to twelve watts. The second mechanism was an electric match, DuPont S-65 squib. The squib was stripped of its insulation, re-insulated with ceramic heads and positioned at the end of the one inch pipe section. The squib releases four to eight calories in about 20 milli seconds.

## Concentrations

Tests were run at n-hexadecane concentrations from 28 mg./sq. ft. to 6500 mg./sq. ft. The results of tests for surface mobility give a visual idea of the quantity of oil at these levels. At 100 mg./sq. ft. no oil is visible and no smear can be detected when the surface is rubbed with a finger and the area inspected under a bright white light. At 250 mg./sq. ft. the surface has a slight oily appearance but no smearing is discernible after testing as above. At 500 mg./sq. ft. the oil has a definite flow characteristic and a slight smear can be detected. At 1000 mg./sq. ft. smearing is considerable and at 2500 mg./sq. ft. the oil can be pushed with your finger.

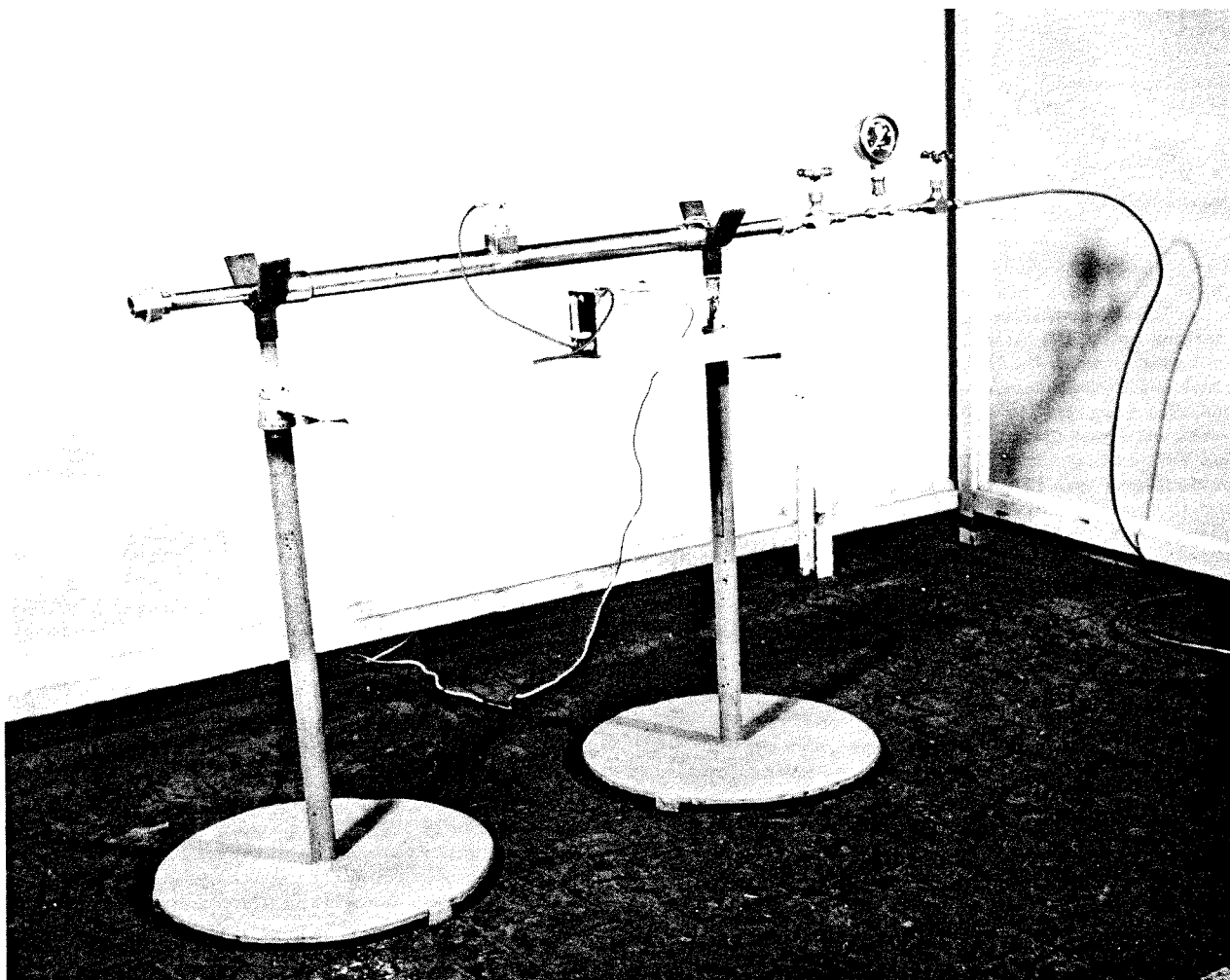


Figure 3. Ignition apparatus using gaseous oxygen.

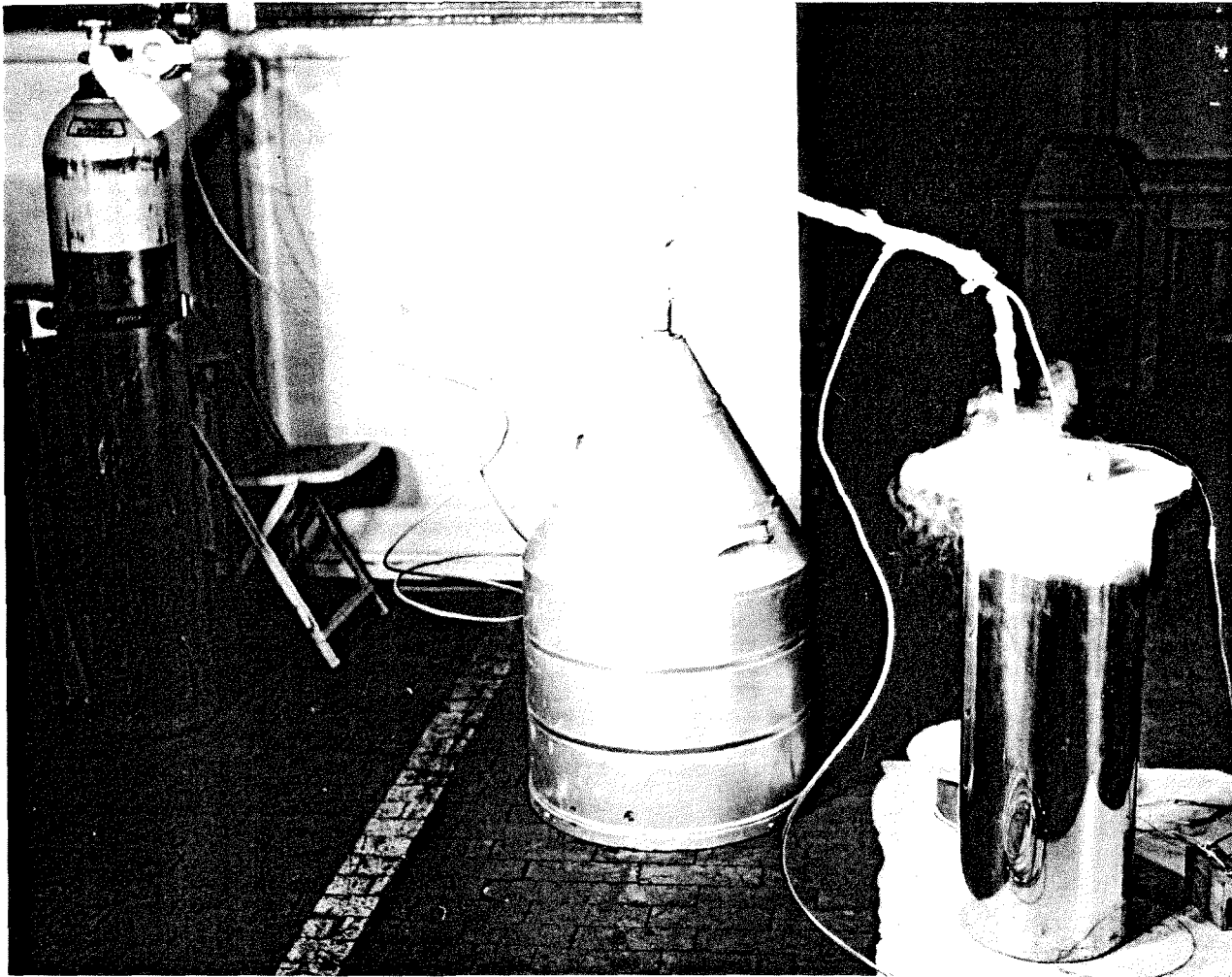


Figure 4. Ignition apparatus using liquid oxygen before ignition.

No discernible reactions occurred at concentrations below 1000 mg./sq. ft. and 200 psig. A burn spot was found at the point ignition was applied but combustion had not propagated. At 1050 mg./sq. ft. and 1500 psig ignition occurred. A bright ring was observed in some instances that indicated that combustion had begun but had not propagated outside of the immediate area. In ten runs made at 1050 mg./sq. ft. and 1500 psig recovery was about 83 per cent compared to a recovery of about 99 per cent for ten runs at the same concentrations and pressures from 50 to 200 psig.

At 6500 mg./sq. ft. and 50 psig detonations were produced. These were the only times that the rupture discs on the pipe section burst.

### Freezing and flaking

The ignition tests would tend to indicate that concentrations up to 1000 mg./sq. ft. would be acceptable. However, as noted previously, surface films of 500 mg./sq. ft. and greater began to show definite flow characteristics. These film concentrations would tend to flow to and concentrate in low portions of a system and increase the hazard of ignition at these locations. This, of course, would be intolerable in any process equipment. Also, in a cold system, the film tended to freeze and flake off at concentrations above 500 mg./sq. ft. With a hydrocarbon such as n-hexadecane,

which is lighter than liquid oxygen, these flakes float and concentrate on the surface. These two phenomena, the flow characteristics and the freezing and flaking in a cold system, require the reduction of a maximum safe concentration to something less than 500 mg./sq. ft.

### An indicated safety

For hydrocarbons with the same characteristics as n-hexadecane, it would appear that a safe maximum level of film contamination could be set at 100 mg./sq. ft. It is, of course, recognized that additional work is required to firmly establish this level.

A final note can be made concerning the sources of ignition that were used. From the literature it was estimated that the oxygen-oil mixture required a minimum ignition energy of  $6 \times 10^{-3}$  calories. The power input to the spark coil produced a spark of about 20,000 volts for 10 seconds. This is in the same order of magnitude as friction or impact effects that may be experienced in process equipment. The rate of application of energy by the electric squib, four to eight calories in 20 milli seconds was several orders of magnitude greater than that by the spark system, and it is doubtful that any source of ignition as powerful would ever exist in a practical process system. Comparatively few tests were run with the electric squibs. Little difference in results were noted between the two ignition systems except for poorer reproducibility of results with the squib. (Note: More complete details on

experimental technique can be found in the paper presented by Dr. Ephriam Kehat at the Cryogenic Engi-

neering Conference, Ann Arbor, Michigan, August 15-17, 1961.)

## DISCUSSION

LOGINOW—U. S. Steel: When you mentioned flowing of these hydrocarbon films, is this flowing under the influence of an air pressure or a gas flow or is this free-flowing in a stagnant condition?

BALL—Air Products & Chemical: The tests that we ran were in a stagnant condition. The laboratory tests consisted of coating a flat plate with a known concentration of hydrocarbon and leaving this plate in a vertical position for a period of twenty-four hours. It was then inspected visually for any change of the concentration on the plate itself. One of the things that we hope to test later on is the same sort of measurement in a flowing stream. I might make one comment which relates back to the previous discussion. I indicated in this paper that we did use carbon tet for this purpose. At Air Products, the only place that we do use carbon tet is in the laboratory. We don't use it in the process plants. For the actual cleaning of our process equipment, we use, for the most part, methylene chloride.

LAWRENCE—Armour Agriculture Chemical: How did you extract the oil and how did you measure it?

BALL: We washed the surfaces after coating or after the actual test, using two different washes of carbon tet. Then we concentrated the combined washes and measured the concentration of oil with an IR-4.

LAWRENCE: You actually measured what you washed out, and you assumed that you washed it all out?

BALL: That is right.

HEPP: You state in here that 100 mg. appears to be safe, and yet the Air Force use four mg. Is the difference between four and 100 significant from a process standpoint, or is this something to do with the missile field?

BALL: I believe that when we get up to the range of 100 milligrams we are getting into a level of contamination that can be procured by the normal shop practices. There is a lot of work that has to be done on this particular program. We feel that we really are just beginning to get some of the data that would be helpful from a manufacturing standpoint and also from a practical standpoint in an operating plant.

## GENERAL DISCUSSION

TIXHON: I would like to know what is the average life of the seal in a high pressure oxygen pump? We have had trouble at the start-up with our high pressure pump.

PORTER—Dominion Foundries & Steel: We have a Byron-Jackson oxygen pump operating at 425 pounds pressure. We take these seals apart every two months and clean them up, and we haven't actually changed one for two and one-half years. We just clean them up and put them back into service. We use a Dow Chemical grease, and the pump is greased twice every eight hours, and we haven't had to change the seal in over two and one-half years.

FUNK: We normally give specifications for the rock wool to be used. This concerns density. It concerns sulfur content. It concerns hygroscopic properties and it concerns also the maximum concentration of combustible materials. We allow three-tenths percent on the combustible materials. Now we found out that Perlite can have five-tenths up to eight-tenths percent on combustible materials and we consider this as a problem.

WALKER: We recently went through a fairly nasty shutdown to find a leak where we are involved in digging out glass wool which was very heavily packed. Has anyone had any further experience on using Perlite or Vermiculite as insulation which would be more easily removed, or has anyone discovered a more reasonable way of removing glass wool from the box in order to get a strictly localized leak? It was a leak in our high pressure nitrogen cooling which involved going into the box at several points in order to locate the leak. Now with glass wool, it is hard to tell where the leak is coming from unless you are lucky enough to find it right at the beginning. We had a suspicion of where it was. As it turned out, we were right; but we dug in several places before we actually found the leak. Had it been some easily removable substance, we could have cut down our shutdown time considerably.

BOLLEN: I admit that rockwool insulation has its disadvantages when it is necessary to remove it from the cold box but at least it is possible to remove only part of the insulation from isolated sections in order to carry out minor repairs. In the case of Pearlite or other similar materials usually it is necessary to remove all the insulation from the cold box.

HEPP: We had rock wool in our hydrogen box and we switched to Perlite to enable us to empty the box faster, and fortunately we haven't had to empty it completely since we put it in so I cannot comment on how fast we will be able to get it out. We don't have any formalized system of taking it out. If you have any process leaks, you will find them with Perlite because it acts as a sandblasting medium and it will open them up right away. This is not too bad if you want to make sure you have a tight box. We were on stream about a week and, what must have been a small leak enlarged in that week's time to the point that we had to shut down. Once we fixed that up and went back on stream, we have had no difficulty. Perlite was advantageous to us also in that we had to only lower the level down to where the leak was, which was high in the box.

WALKER: What method do you use to put the Perlite into your box?

HEPP: At the top of the box, we have two chimneys. They are just twelve-inch pieces of pipe, and we just dump it in. It flows very readily and you have no trouble packing or anything like that. You do find, after you have been on stream that you have to keep filling these chimneys up. It settles, keeps settling, and is still settling.

SHANER: We have used Perlite extensively in our cold boxes for about the past ten or twelve years. (Well in excess of fifty plants). One of the chief problems that you have to recognize and be able to cope with is the infiltration of moisture into the Perlite. To insure

this we have gone to circular casings which are completely welded. In other words, we have done away with the flat casing type construction with the bolted plates. If you can keep the Perlite dry, then you can remove it much more easily than you can if you have moisture infiltrating into it.

LaRUE—Spencer Chemical: We have an argon plant where we have magnesium carbonate in a circular cold box. We have opened it a number of times and we don't find it near as fluid as people would expect. In other words, it has packing tendencies and we have been able to go in and make isolated repairs without having to drain the whole thing.

BOLLEN: Do you do any shoring when you have to go into it in that manner?

LaRUE: We did several times and other times it was not necessary. We didn't have to go far but it is not near as fluid as some people think.

VARNEY—Johns-Manville: We presently have a test cold box at our research center and we are evaluating several insulations—Perlite, rock wool and synthetic calcium silicate for handling qualities and for the abrasive factor. We should have some reports on these within the next few months.

WELLS: When the plant goes down, we will hold liquids for two hours. This is a limit that has been established since we started up. We do this without regard to the concentration of contaminants. Previously, I think it has been reported that one plant would hold liquids for not more than about fifteen minutes and others would hold them for as long as a week. We have been considering changing our approach to the problem to at least a basis that considers the amount of evaporation and the contaminant level. Most of the time such a basis would extend our holding time, and could considerably reduce the downtime. If we dump the liquids, it takes a lot longer to get back on stream than it does if we retain the liquids to start back up with. I would like to hear how some of the other people approach this problem.

GIBSON: We have two air plants supplied by two centrifugal compressors in parallel at about 80 pounds pressure. On a few occasions one compressor has been shut down and we have maintained both plants at reduced pressure—approximately forty pounds. This has kept us operating for as long as two hours without either holding or dropping out the plant.

SHANER: We find that we can hold liquids indefinitely as far as the shutdown of the plant is concerned. We can do this for two reasons; one is the design of our main condenser is unique in that we have a continuous recirculation of the liquid through silica gel, and this continues even when the plant is shut down so that we can maintain the liquid as a clean liquid for a considerable length of time after the plant is off stream.

Secondly, we can add fresh liquid to maintain a given liquid level from our large liquid production, storage and distribution system so the plant can be kept cold for an indefinite period.

FUNK: The liquid holding time depends upon the size and type of the plant of course, but to be sure you will do the right thing, you should follow up with analyses. We have held liquids as long as forty-eight hours without risking anything.

HOFMAIER—American Cyanamid: What do you call frequency on this liquid analysis?

FUNK: I might say that frequent intervals are one or two hours. In some plants, the liquid evaporates fast in the main condenser and then you would have to check more frequently.

BOLLEN: Our air separation plant is a relatively small one and we have found that if we leave it down for anything longer than a few hours the air going through the box following start-up will be warm enough to affect the vaporizer sections. The liquid oxygen level which has been retained quite nicely throughout the shutdown will drop rapidly indicating rapid vaporization of the liquid and therefore concentration of any hydrocarbons that may be present in the liquid oxygen. If the cold box has not been down too long the liquid oxygen level builds up fairly quickly again to restore hydrocarbon concentrations to their normal level. Never-the-less it does point up the need to maintain close vigilance of hydrocarbon concentrations during such start-ups. The hydrocarbons in the liquid oxygen in our air plant are continuously monitored by an M.S.A. total hydrocarbon analyzer. This is supplemented by laboratory analyses of spot samples of oxygen taken from the vaporizer section during such start-ups.

JENKINS: I think the main problem is how much liquid oxygen do you have left when you get back on stream. In other words, if you have a certain level, say 30% in your vaporizer, and you know it is going to take 20% to get back on stream before you start building level again, I would say you are in dangerous position. But if you have 100% level, I don't feel you are in too dangerous a position as long as you continue to analyze. As long as you make sure that you don't approach a dry condition on start-up, and maintain analyses all the time, I don't see too much danger.

WEIGERS: When a plant is shutdown you can gain a good deal of safety if you transfer all liquids from the high pressure sections into the main condenser reboiler. Depending somewhat on plant design, the transfer of this liquid can just about dilute the main condenser-reboiler volume by 50% (or double the volume). This gives you a good bit of safety and prolongs the time before you reach a potentially dangerous level of contamination on your shutdown.