

Statement of A.B. Savage as to Sinclair Contention Number 4:

Conclusions:

The corrosion and sludging of condenser tubes by pond water may induce leakage of pond water of variable composition into the water of the secondary cooling system at a driving force of perhaps 50 psig.

A much more serious cause of steam generator corrosion, particularly of that unit which supplies steam to The Dow Chemical Company, will be careless operation of the cation and anion exchanges, very common in the chemical industry, the use of ammonia for neutralization and of hydrazine for oxygen scavenging, and failure to establish adequate controls for when blowdown should be performed.

Contact of dissimilar metals of the tube and shell components of the steam generator with the electrolyte will set up corrosive couples.

Such couples, chemical components and mechanical stress will aid in the initiation of intergranular corrosion. The chemicals chosen are not well suited to the materials of construction.

Stress during construction and because of expansion and vibration, liquid and vapor impingement at high velocities, transients and high pressures during operation will contribute to steam generator tube failure at a driving force of 1,000 psig.

Such tube failure will necessitate shutdown of the unit. The shutdown procedure in the Ginna system (NUREG 0537) was haphazard and erratic. Considering the narrow margin of safety as to potential pressure, the result could have been a disaster.

The incidence of tube failures in steam generators is increasing with time.

Improved materials of construction, improved design and fabrication and improved water chemistry are needed before permission is given for any more units to start up.

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Reference is made to attachment C in the testimony of C. Hillman. The sketch is inadequate and confusing.

1. Primary coolant.

The primary coolant is shown circulating up through the reactor, down through the tubes of the boiler, and through a centrifugal pump back to the reactor, at a stated pressure of 2,000 psig. Any gases will tend to accumulate above the upper tube sheet in the generator.

2. Steam flow.

Feed water is introduced into and preheated in the lower annulus of the generator, vaporized in the shell, and the steam leaves the upper annulus of the generator below the top. The steam flows to turbo-generators in tandem, where it expanded and ultimately condensed under vacuum conditions, and is recycled by a centrifugal pump through a "full-flow" demineralizer and back into the annulus of the generator.

3. Condensation.

The vapor leaving the turbines is condensed in the shell of the condenser under vacuum, as evidenced by the hot-well. Cooling water (service water) from the pond passes through the tubes of the apparently horizontal condenser, and is returned to the pond.

4. Steam sold to The Dow Chemical Company.

In NUREG 0537, steam production of from 1.4×10^6 to 4.05×10^6 pounds of steam per hour is stated, or from 46.5 gal./sec. to 134 gal./sec., or perhaps an average of 109 gal./sec. of feed water. It is stated that reactor #2 will produce 825 MW, reactor #1 504 MW of power, and thus the difference, 148 MW of power equivalent will go to steam:

3.6×10^6 lb./hr. at 175 psig., plus

0.4×10^6 lb./hr. at 600 psig.

The point where the steam is withdrawn is not stated. One may suppose that the steam is withdrawn interstage between two turbogenerator stages:

- (a) Stage 1. Expansion of steam at 1,000 psig. (approximately 575°F) to 600 psig. (approximately 485°F) through a turbine; and
- (b) Withdrawal of 600 psig. steam for Dow at this point.
- (c) Stage 2. Expansion of steam at 600 psig. (approximately 485°F) to 175 psig. (approximately 375°F) through a turbine;
- (d) Withdrawal of 175 psig. steam for Dow at this point.
- (e) Stage 3. Expansion of steam at 175 psig. (approximately 375°F) through a turbine to 20 inches of mercury vacuum, 190°F.
- (f) Condensation of the remaining steam at this pressure.
- (g) The vacuum could be maintained by an Ingersoll-Rand type steam jet powered vacuum unit, discharging through the hot well, and removing air from the system.

5. Makeup.

Perhaps 80 per cent of the steam sold to Dow would be returned as condensate and reused. The balance would be made up from fresh water, amounting to a maximum of 810,000 pounds per hour, or 97 gal./sec. This amount of water would be passed through ion exchange purification units. It would also be used for makeup to offset any leakage from the primary or the secondary cooling system.

6. Water quality.

(a) Pond, or service water.

The water pumped from the pond will contain algae, salts, rust and other contaminants from The Dow Chemical Company's upstream operation, sediment, small fish and other materials. Hopefully it will have been passed through a set of bars and through a magnetic separator. The listed materials may be expected to collect behind the tube sheet on the inlet side of the condenser and to contribute to its corrosion. As the pond water will come from the Tittibawassee Reiver, it will contain perhaps 30 ppm. of NaCl. One of the upstream tributaries, the Salt River can contain as much as 90 ppm. of salt. Otherwise, the river comes from a sandy, low mineral area. It may contain organic materials from the forest floor, salt from highways, agricultural contaminants, etc. The volume of the pond is not stated, so concentrations are uncertain. Doubtless they vary widely. Concentrations will depend upon the volume, upon the relative locations of inlet and withdrawal sites, and upon the amount of blowdown discharged. The pond will contain acid and alkali from ion exchange unit regeneration and all of the ions that had been removed by the exchangers. The pH will vary.

It was estimated some years ago that the equivalent of the entire river flow passes through the plant of The Dow Chemical Company several times before continuing down the river. In any case the pond water will be corrosive and will tend to carry sludge.

(b) Water supply for ion exchange.

It is intended initially to use Midland city water (Huron water would serve as well) as makeup, and after the first year to use ion exchange water from The Dow Chemical Company. The Saginaw-Midland Water Authority takes water from a crib several miles out in Lake Huron at Whitestone Point and pumps it about 140 miles. The crib intercepts a Lake Superior current that is low in impurities because it comes from a granite bed. The Dow Chemical Company uses raw Huron water in several operations. According to the Midland water plant laboratory, city water and Huron water have much the same typical composition, differing chiefly in pH:

Ions	Huron	City
Na ⁺		
Ca ⁺⁺	2 ppm.	4 ppm.
Mg ⁺⁺	26	30
Cl ⁻	8	8
	12	15
SO ₄ ⁻⁻	30	20
pH	7.9	9.0-9.4

The Huron water is limed to reduce hardness, treated with chlorine for purification, and fluoridated.

(c) Cation exchange water.

The Dow Chemical Company passes Huron water through a cation exchanger operating on the Na⁺ cycle. This removes all heavy metal ions, replacing them with Na⁺ ions. The exhausted exchanger is regenerated with NaCl solution and washed. From a cation exchanger on the Na⁺ cycle fed with Huron water one might expect:

Na ⁺	28 ppm.
Cl ⁻	14
SO ₄ ⁻⁻	25

pH 8.6-9.1

(d) Hydrogen ion cycle.

In order to be able to obtain the equivalent of distilled water, the first step cation exchanger must be operated on the H⁺ cycle, that is, it must be regenerated with strong acid, for example with H₂SO₄, rather

than with salt, and washed. One might expect from Huron water:

HCl	14.5 ppm.
H ₂ SO ₄	25.6

pH 6, approximately

When a cation exchanger of either type is exhausted, Na⁺, Ca⁺⁺, etc. ions will pass through, and it must be regenerated. It is the commonest thing in the world for operators to permit this to occur. The output of acids from the operating exchanger depends upon the anions present: HCl, H₂SO₄ and H₂CO₃ for example. Different resins are used for weak and for strong acids.

(e) Anion exchange water.

An anion exchanger does not exchange ions, but, instead, absorbs acids (or if intended for bases, it absorbs bases) as such. The product is essentially pure water. When the exchanger is exhausted, acids pass through. This results in a drop in pH and an immediate increase in specific conductance. However, it is common for operators to not notice this. Some specific conductances of ions at 25°C, include:

H ⁺	349.8	Cl ⁻	76.3
Na ⁺	50.1	OH ⁻	198.0
½Ca ⁺⁺	59.5	½SO ₄ ⁻⁻	79.8

The specific conductance due to HCl is thus, for example, about 3.4 times that due to NaCl.

The anion exchanger is regenerated with NaOH or with Na₂CO₃.

(f) Other considerations.

If city water is used, it will contain chlorine, which is not removed by an exchanger. The fate of F⁻ ions is uncertain.

Water, consisting of returned condensate and fresh water makeup, will be demineralized and stored. It will be introduced into the secondary cycle, which also contains so-called "full-flow polishing" demineralizers. These, too, can exhaust and pass cations and acids. Ions passed will accumulate in the steam generator and can only be removed by blowdown. Meanwhile they will corrode the equipment.

Ion exchange resins can be subject to cracking of the beads and to erosion. Eventually resin will enter the steam generator, whether due to erosion or to excessive velocity of the feed water. No mention is made of a polishing filter to retain resin. Cation resins contain acidic groups. Anion resins contain basic groups. If cation resin enters the anion exchanger, the result is uncertain. Resins must be added or replaced after long usage.

(g) Other chemistry.

It is stated that ammonia will be used for pH control and hydrazine for scavenging oxygen. NUREG 0571 says that hydrogen will be used. Ammonium chloride is very corrosive. It hydrolyzes to an acid pH. Hydrazine hydrochloride or sulfate will be corrosive. Silicate, if present, might reduce corrosion.

7. The steam generator.

The Babcock and Wilcox once-through steam generator has primary coolant on the tube side and secondary coolant on the shell side. The secondary coolant is preheated in the annulus and converted to steam in the shell. NUREG 0571 states that the tubes are of Inconel, 0.625 inch O.D., 0.035 inch wall thickness. If one assumes a factor of safety of 6, the working pressure of the tubes is about 1,500 psig.

Inconel, a product of International Nickel Company, contains:

Nickel	79.5%
Chromium	13.0
Iron	6.5
Carbon	0.08
Copper	0.20
Manganese	0.25
unknown	0.47

Of these components, copper is undesirable; iron less so. I am not certain whether Inconel is a developed alloy, or whether, like Monel, it is a composition found in natural ore. Inconel resembles stainless steel 316 in many properties.

Inconel has only partial resistance to NH_4Cl , to $\text{Ca}(\text{OCl})_2$, to Cl_2 , to HCl , to H_3PO_4 and to $\text{Ca}(\text{OH})_2$, as well as poor resistance to FeCl_3 , according to Perry's Chemical Engineer's Handbook. Tube failures have occurred when phosphates were used initially in the system.

(a) Pressure. The pump pressure to the reactor is stated to be 2,000 PSIG., in order to prevent vaporization in the reactor. The working pressure of the generator tubes is stated above to be about 1,500 psig. Steam is to be produced at 1,000 psig., or about 555°F. The pressure temperature relationship for water includes:

Temp. °F	Pressure, psia.
555	1015
600	1543
640	2345
700	3093
705.4(c)	3206.2(c)

Should the primary water temperature rise from near 555°F. to 640°F., it is questionable whether pump pressure could be maintained. Should it rise to 705.4°F., the critical point, the reactor would run away. Tube failure in the steam generator could occur for chemical or for mechanical reasons. The driving force for leakage to the secondary side would be 1,000 psig.

(b) The corrosion resistance of metals such as nickel and stainless steel depends upon the formation of a passive film of oxide or the like upon the surface. This is initially established by oxygen and promoted by alkaline conditions. In an oxygen-free atmosphere, if it is lost, it cannot be reestablished. Chloride and sulfate ions interfere with passivity.

(c) When dissimilar metals are in contact with an electrolyte, a galvanic couple is formed and a potential set up. The metal at the higher potential will be the anode and will tend to go into solution. Couples can occur between dissimilar metals, between an alloy and undispersed components of it, between dissimilarly heat-treated metals and between metals that have experienced dissimilar stress. Inconel contains copper, for example. Copper not only sets up a couple, but it is dissolved as a complex by ammonia. A welding rod of the wrong composition, such as a Monel one, might have been used. If the metal has a crystalline or a granular structure, corrosion can begin at the interfaces between crystals. A few single electrode potentials include:

Fe/FeSO_4	-0.44
Ni/NiSO_4	-0.23
Cu/CuSO_4	+0.34

(d) The water in the primary cycle will contain impurities that occur in the initial feed water, or in water introduced to replace leakage and blowdown. Besides the initial components of the feed water, it can contain metallic components of the reactor, the generator, the piping and the pump. I have not seen a stuffing box nor mechanical seal on a pump that will not leak sooner or later. Gases and vapor will collect above the tube sheet in the generator.

(e) Secondary cycle.

As one unit is to produce steam for sale, the secondary cycle of that unit will be more subject to corrosion than will that of the other unit. There will be a buildup of ions from the feed water and from ion exchange operations, and from chemical treatment: acids, chlorine, cations, anions, air and contaminants from the materials of construction. These will be removed by blowdown. The shell side of the steam generator is stated to contain iron baffles as spacers and supports. These and the shell are subject to corrosion and to electrolysis. There is no mention of attached anodes. Sludge will collect on baffles, supports and the lower tube sheet. As steam is removed, these will concentrate, and blowdown will be necessary. It is essential that all construction debris shall have been removed. The driving force for leakage will be 1,000 psig. A critical point of corrosion will be at the liquid-vapor interface, and in the area above this where entrainment occurs. The vapor velocity will be much greater than the liquid velocity.

8. The condenser.

Nothing is said of the construction of the condenser, but for operation at perhaps 20 inches of mercury vacuum, 190°F and with nominally salt-free water on the tube side, it may be assumed to be of conventional iron construction. Corrosion products will develop in the shell, and remain there, or pass into the hot-well.

The tube sheets and tubes will be corroded and sludged up by components in the cooling pond. In case of a leak, these will be sucked into the shell and pass into the hot-well, from where they will enter the secondary water system. The driving force for leakage will be about 50 psig. Fouling of this condenser will be extensive, but, aside from leaks, the chief danger to the secondary water supply lies in the uncertainties of ion exchange operation and chemical control, and improper materials of construction.

Admittedly, 3400 tons per year of sulfuric acid, presumably 66° Be., or 775 pounds per hour will be used to regenerate the cation exchangers and will enter the pond, partly neutralized.

9. Mechanical.

The Babcock and Wilcox steam generator differs from others in having two rigid tube sheets, rather than hairpin tubes fixed to a single sheet. It should be relatively free from vibrational stress and accompanying wear, but suffers from lack of provision for thermal expansion. A floating tube sheet, occasionally used, is not practical. If the tubes are straight and rigid at room temperature, they will expand and be bowed at operating temperature. Conversely, if they are rigid and straight at operating temperature, they will be drawn at normal temperature, perhaps beyond their proportional limit. It is not stated, but the tube sheets are probably drilled. Boring, or broaching (in the sense of burnishing) would give smoother contact surfaces. When the tubes are expanded to fit the holes in the tube sheet, the stress exceeds the proportional limit and thereafter they are liable to further expansion under stress. If the tubes are expanded only on the outer side, crevices will surround the tubes on the shell side and corrosive components can build up. If the tubes are expanded through to the shell side, it makes their removal more difficult and strains extend further into the shell. In either case the stress on a slender column under axial load is added

to the stress of pressure. Stresses will initiate intergranular corrosion of the tubing.

Should a tube fail, it would be a cantilever with one fixed end. It would vibrate and rub, both against other tubes and against the tube supports, although not as much as in other designs.

The Babcock and Wilcox tube spacers are broached, rather than drilled. If by broaching is meant burnishing, they would present fairly smooth contact surfaces.

NUREG 0571 indicates tube failure due to fatigue near the top of the generator, that is, near the liquid-vapor interface or in the vapor space. Stress is caused by vibration of the tubes in the vapor space plus column action and corrosion at the interface.

Foreign material can collect at the tube sheets and supports, and could wear the tubes. Construction residues must be completely removed.

The tubes can be dented by foreign bodies, or thinned by stress and corrosion. If faulty tubes are plugged, the resulting flow currents may erode nearby tubes.

So-called "sleeving", that is the placement of a piece of smaller tube inside of a stressed tube at the tube sheet, and expansion to provide tightness, is not a desirable procedure. It further stresses the tube, and increases velocity through the sleeved area, and may cause cross-currents above the tube sheet.

10. Other comments.

In the case of generator tube rupture, primary cooling water will leak into the secondary system at 1,000 psig. driving pressure, resulting in some loss of cooling and introducing some radioactivity. Shutdown for repair will be necessary.

It is obvious that the use of pond water for emergency cooling will contaminate both the reactor system and the pond.

Clearly the best way to cool a reactor would be to lower the control rods, to keep the liquid level above the rods and to remove vaporized steam. Steam removal would provide $2\frac{1}{2}$ times the heat removal per pound of water that liquid cooling would, as a minimum. NUREG 0916 indicates that the aplomb of the operators in the Ginna plant tube failure event resembled that of a cat on a hot stove, with little attention to engineering principles, and continuous indecision.

Steam evolved in an emergency could be directly condensed with water sprays in a suitable vessel and the inert gases vented.

A serious source of atmospheric contamination is the use of pop valves for relief. Such valves are subject to wire-drawing and generally do not reseal properly. They are unsatisfactory for use where toxic vapors and gases are involved. Parallel frangible safeties, with their stems locked together so that if one accessible, the other is not, would be much safer.

The air-operated venting valve in the primary system is inappropriate. First, it can be valved off by a blocking valve, which would make it ineffective and might cause transients if closed suddenly, and, second, if it is direct acting, air failure would close it, even if needed, and, if reverse acting, air failure would open it, causing unwanted venting, equally bad. Closure of valves to the turbine would cause transients.

Finally, the discussions of steam tube integrity and the studies at Brookhaven and the Franklin Institute are excellent.

My name is A.B. Savage. I am a retired Dow Chemical Company research engineer. I do not speak for the company, nor have I used its facilities in this matter.

I attended the University of Minnesota and received the degree of Bachelor of Chemical Engineering with Distinction in 1935. Courses of special relevance included resistance of materials, metallography, industrial electrochemistry, electric power and mechanical engineering. I was elected to Tau Beta Pi, honorary engineering society, and to Phi Lambda Upsilon, honorary chemistry society.

I had a fellowship with and worked in the plant of the Minnesota and Ontario Paper Company, now owned by Boise Cascade, 1935-1937. I received the Degree of M.S. in Ch.E. and was elected to Sigma Xi, honorary research society. Experience included reactions involving corrosive acids under pressure, pH control and the observation of evaporator operation and maintenance.

I worked as a research chemical engineer under various titles for the Dow Chemical Company for 39½ years. I was an active member of the American Institute of Chemical Engineers and the American Chemical Society. I was elected to the Research Society of America. Experience included operation of reactors at about 500°F, operation of reactors at about 200 psig., operation of ion exchangers, water quality, pH, conductometric and potentiometric measurements, removal of salts from products and regulating their pH, testing for corrosion, and design and operation of continuous and batch stills, condensers and heat exchangers, and operation of a process involving corrosive acid under pressure. I also had to do with prevention of possible runaway reactions, and many aspects of safety, including frangible safeties, relief valves, etc. I took a course in continuous reactor design from a University of Michigan instructor.

I hold more than 40 U.S. or foreign patents and have written technical book chapters and encyclopaedia articles.