Met-Ed GPU

Metropolitan Edison Company
Post Office Box 542
Reading Pennsylvania 19640
215 929-3601

Writer's Direct Dial Number

October 16, 1979
GQL 1234

TMI-2 Support
Attn: R. Vollmer, Director
U. S. Nuclear Regulatory Commission
Washington, D.C. 20555

Dear Sir:

Three Mile Island Nuclear Station, Unit 2 (TMI-2)
License No. DPR-73
Docket No. 50-320
RCS Corrosion/Chemistry Program

In response to your letter of September 17, 1979 concerning primary system chemistry and corrosion program the following information is provided:

The primary item of concern related to Reactor Coolant System (RCS) Chemistry/Corrosion control is chloride stress corrosion of austenitic stainless steel. This concern is centered around the potential for rapid corrosion cracking if the variables for chloride stress corrosion are allowed to reach applicable values. The variables of concern are: time, temperature, stress, chlorides, oxygen and pH.

The temperature at which chloride stress corrosion occurs is not well defined. The plant is presently at an average core temperature of about 170°F.

At this temperature, the possibility of chloride stress corrosion may still be of concern. When the Mini-Decay Heat Removal system is placed into operation primary temperature will be reduced to less than 140°F to further reduce the possibility of chloride stress corrosion.

Chlorides in the RCS are higher than desirable (3-5 ppm recently). They have not been controlled because of the lack of purification capability and the undesirability of feed and bleeding due to the large quantities of radioactive water which would result. Chlorides are controlled to the extent possible by limiting the concentration in the RCS makeup water to 1.0 ppm.

RCS dissolved oxygen is controlled by maintaining a hydrogen inventory of 5-15 cc/kg the limit for oxygen in the RCS is .1 ppm. Oxygen is maintained at less than this value to minimize the possibility of chloride stress corrosion and general corrosion. Difficulties have recently been experienced in maintaining continuous operation of the makeup water vacuum degassifier, due to leakage of solenoid valves in this system. As a result of interruption of makeup deaeration, approximately 2600 gallon of 4.5 ppm oxygen bearing makeup have been added to the RCS over the last three weeks. Corrections of these difficulties are being pursued presently with high priority.

A001
S 1/1

1185 263

7910190298

Metropolitan Edison Company is a Member of the General Public Utilities System

RCS pH is maintained ≥ 7.5 which provides for a margin of .5 pH units above the pH of 7.0 referred to in Section 6.1.1 of the NRC's standard review plan concerning pH for post LOCA core cooling water.

Further information on plant conditions, chemistry and corrosion control is contained in the attached B&W TMI-2 water chemistry recommendations and requirements.

Sincerely,

J. G. Herbein
Vice President-Nuclear Operations

JGH:LWH:tas

Enclosures

TMI-2 WATER CHEMISTRY

1. GENERAL

This document provides information on B&W's recommendations and requirements for the water chemistry at TMI-2, with the following conditions:

a) Condition A -

Reactor coolant system in natural circulation at pressures in the range of 100-300 psig and temperatures of approximately 100-180°F with one steam generator operating under a vacuum or in a solid condition to remove decay heat and letdown and makeup via the makeup and purification system.

b) Condition B -

Reactor coolant system at pressures of approximately 70-100 psig and temperatures of approximately 100-130°F with the "Mini"-decay heat cooling system operating to remove decay heat, the steam generators isolated and the standby pressure control system operating for RCS pressure control and fresh RC makeup additions.

2. REACTOR COOLANT SYSTEM (RCS)

2.1 General

The RCS water chemistry specifications for both Conditions A and B are as follows:

pH at 77F	≥7.5
Boron	3000-4000 ppm
Hydrogen	5-15 std cc/kg
Chloride	See Section 2.4
Fluoride	See Section 2.5
Oxygen	See Section 2.6
Sodium	See Section 2.2

2.2 pH and Sodium or Sodium Hydroxide

The pH must be maintained at ≥7.5 in order to minimize the possibility of chloride stress corrosion of austenitic stainless steel. While a specific upper limit is not listed, an effort should be made to keep the pH below 9.5. It is also recommended that the pH should actually be maintained at ≥8.0 in order to assure that the pH is ≥7.5 at all times. The pH is adjusted by the use of sodium hydroxide additions to the RCS. The relationship between pH and caustic concentrations for various boric acid concentrations are shown in Figure 1, while the graph is for solutions also containing 1 w/o sodium thiosulfate, the presence of the sodium thiosulfate does not have **any significant** effect on the pH.

The pH limit of ≥7.5 at 77 F is also a technical specification limit.

2.3 Boron and Boric Acid

The boron range of 3000-4000 ppm is equivalent to a range of 17,000-22,800 ppm as boric acid and this range is specified to maintain a subcritical condition for the postulated fuel configurations in the vessel region. Actually, however, B&W recommends that the actual boron or boric acid concentration be maintained on the high side of the specification range to provide a further assurance of a subcritical condition at all times with a slow mixing rate in the RCS.

The technical specification for boron is 3000-4500 ppm with the upper limit based on the solubility limit of boric acid at 32 F.

2.4 Hydrogen, Oxygen and Hydrazine

A dissolved hydrogen range of 5-15 std cc H_2/kg water is specified to help control oxygen that may result from the radiolysis of the coolant or that may come in with the fresh makeup. A hydrogen concentraction somewhat in excess of 15 std cc/kg water does not create any problems. Up to now, the hdyrogen has been "self-sustaining" since the March 28 incident, i.e., it has not been necessary to make any adjustments to maintain a dissolved hydrogen residual of 5 std cc/kg. In the event that hydrogen control becomes a problem, hydrazine additions should be made to indirectly increase the hydrogen concentration for the temperatures in the RCS at Condition A and Condition B, the reaction rate between hydrazine and oxygen is slow, but the reaction rate is more rapid in radiation field which makes the hydrazine an effective RCS oxygen scavenger even though the radiation field causes the hydrazine to decompose. Hydrogen is a hydrazine decomposition product in a radiation field with the amount generated being dependent on whether the solution is aerated or deaerated as shown below:

$2N_2H_4 \longrightarrow 2NH_3+N_2+H_2$ (deaerated solution)

$N_2H_4 \longrightarrow N_2+2H_2$ (aearated solution)

For every pound of pure hydrazize added to the RCS - the first reaction forms about 0.6 cc H_2/kg water in the RCS whereas the second reaction forms about 2.3 std cc H_2/kg water in the RCS.

Oxygen is undesirable in the RCS because it promotes the general corrosion of RCS materials, but the real concern is that oxygen is a factor in the chloride stress corrosion of austenitic stainless steels. It's desirable to limit the oxygen to 0.1 ppm max for this reason.

2.5 Chlorides

As stated in Section 1.2.2, chlorides can cause stress corrosion cracking of austenitic stainless steel and is dependent on temperature, stresses, time, chlorides, oxygen, and to some extent, pH. The temperature ranges for Condition A and Condition B are in a borderline area where the possibility of chloride stress corrosion is still of concern and cannot be completely ignored. Therefore, the chlorides should be controlled to the extent possible. The chlorides are controlled by limiting the chlorides in the makeup water to the RCS to 1.0 ppm max.

2.6 Fluorides

As with chlorides, fluorides can cause stress corrosion of austenitic stainless steels and should be controlled by limiting the fluorides in the makeup water to the RCS to 1.0 ppm max.

3. RCS SUPPORTING SYSTEMS - CONDITION A

When the RCS is operating at Condition A as defined in Section 1, the supporting systems can vary particularly from the standpoint of the source of the fresh makeup water (i.e. RC bleed holdup tanks, BWST, etc.). Hence, rather than specify the chemistry for all of these various sources, only the general requirements for the fresh RCS makeup are covered here, and these requirements are identical to those listed in Section 4.3.2 for the charging water storage tank.

4. RCS SUPPORTING SYSTEMS - CONDITION B

4.1 General

This section covers the water chemistry for Condition B when the Mini-Decay Heat Removal System and the Standby RCS Pressure Control System are operating.

4.2 Mini Decay Heat Removal System

When operating, the mini decay heat removal system circulates water directly through the reactor core and thus the system has the same water chemistry as that for the RC System as discussed in Section 2.

4.3 Standby RCS Pressure Control System

The standby RCS pressure control system provides a backup for maintaining the RCS pressure when the need arises. It consists of three surge tanks, a charging water storage tank, a borated water batching tank and associated pumps, valves, piping, and instrumentation. The three surge tanks are connected in series with two tanks completely filled with water and the third tank is maintained under a nitrogen pressure. The charging water storage tank is in effect a makeup tank for the RCS and is the point where chemicals are added to the RCS.

4.3.1 Borated Water Batching Tank

The borated water batching tank is used to makeup the boric acid - sodium hydroxide solution to maintain the specified boron and pH levels in the RCS via the standby RCS pressure control system. When a batch of solution is made up in the tank, the resultant water chemistry is:

Boric Acid	4 wt% nominal
Sodium Hydroxide	0.5 wt% nominal

Demineralized water shall be used in making up the solution.

4.3.1.1 Boric Acid

The 4 wt% boric acid is approximately equivalent to 7000 ppm boron which when diluted in the charging tank by a factor of two will result in a boron concentration of about 3500 ppm which is midway between the 3000-4000 ppm specification for the charging tank and the RCS. The boric acid used to makeup the batch tank shall meet the following specifications*:

Constituent	Minimum %	Maximum %	 ppm
Boric Acid (H_3BO_3)	99.90	-	-
Sodium (Na)	-	0.003	30
Chloride (Cl)	-	0.0004	4
Fluoride (F)	-	0.0004	4
Sulfate (SO_4)	-	0.003	30
Phosphate (PO_4)	-	0.003	30
Iron (Fe)	-	0.0008	8
Heavy Metals (as Pb)	-	0.0002	2
Water Insoluble	-	0.005	50

*United States Borax & Chemical Corporation - Special-Quality Grade Boric Acid and Stauffer Chemical Company - Nuclear Grade Boric Acid meet these specifications.

4.3.1.2 Sodium Hydroxide

As shown in Figure 1 , a solution containing 4 wt% NaOH when diluted by a factor of two (i.e. to 20,000 ppm boric acid and 2500 ppm (0.0625 molar) sodium hydroxide results in a pH of slightly greater than 8.0 at 77F which follows the goal stated in Section 2.2 of maintaining a nominal RCS pH of <8.0 at 77F. The 2500 ppm NaOH concentration is equivalent to about 1400 ppm sodium.

The sodium hydroxide is expected to react with the boric acid and form tetraborate by the reaction:

$$2NaOH + 4H_3Bo_3 \longrightarrow Na_2B_7O_7 + 7\ H_2O$$

Thus, the 4 wt/% boric acid and 0.5 wt/% NaOH mixed in a solution, about 12,500 ppm sodium tetraborate are formed with an excess of about 24,500 ppm boric acid.

Sodium hydroxide added to the borated water batch tanks should be equivalent to rayon grade or equivalent if it is purchased as solution or should be regent grade if it is purchased as pellet or flake.

4.3.2 Charging Water Storage Tank

The charging water storage tanks is the primary source of fresh makeup for the RC system and thus is one of the main control points for controlling the RCS water chemistry. The specifications for this tank are as follows:

Boron	(See Section 4.3.2.1)
pH at 77F	(See Section 4.3.2.2)
Oxygen	0.1 ppm Max.
Chlorides	1.0 ppm Max.
Fluorides	1.0 ppm Max.
Hydrazine	(See Section 4.3.2.3)

Any water added directly to this tank, shall be supplied from a demineralized water source.

4.3.2.1 Boron

The boron concentration shall be that required to maintain the RCS boron concentration in the specified range of 3000-4000 ppm. Therefore, it is prudent to maintain the boron concentration in the charging water storage tank at 3000-4000 ppm. Of course, it may be necessary to exceed this range at times to make proper adjustments to the RCS boron levels.

4.3.2.2 pH

As with the boron, the pH shall be that required to maintain the RCS pH at ≥ 7.5 and preferably at ≥ 8.0. The pH is controlled with sodium hydroxide.

4.3.2.3 Oxygen and Hydrazine

Control of oxygen in the RCS makeup water source is of primary concern because it makes it easier to control the oxygen in the RCS. The recommended oxygen specification for the makeup and consequently the charging tank water is 0.1 ppm max. A hydrazine residual of 300% of the stoichiometric requirements to react with the oxygen should be maintained in the charging water, i.e., if the oxygen level is 0.1 ppm, thus the hydrazine level should be maintained at 0.3 ppm or higher.

As stated in Section 2.4, hydrazine is added when necessary to maintain the hydrogen levels in the RCS. In this case, it will probably be necessary to increase the hydrazine levels in the pressure control system.

The oxygen in the charging tank water is reduced by maintaining water in a heated condition at 180F and spraying the water into the tank.

4.3.3 Surge Tanks

The water chemistry for the surge tanks is the same as that for the charging water storage tanks. The only other consideration is that the nitrogen used to pressurize these tanks should be low in oxygen content in order to limit the absorption of oxygen in to the water. The recommended specifications for oxygen in the nitrogen supplied to these tanks is 0.05 vol. % Max.

5. STEAM GENERATOR FEEDWATER

5.1 General

The steam generator feedwater chemistry depends on whether (1) the steam generator is operating or steaming under a vacuum maintained with a condenser, 2) the steam generator is operating in full solid condition with the feedwater system also operating in solid closed loop condition,

3) feedwater system is in isolated layup condition when the Mini-Decay Heat Removal System is operating to remove decay heat from the RCS.

5.2 Feedwater With Steam Generator Steaming Under Vacuum or with Steam Generator Operating in Full Solid Condition (Condition A)

The specifications for these two operating modes are as follows:

pH at 77F	9.3 - 10.5
Dissolved Oxygen	100 ppb Max.
Cation Conductivity	1μmho/cm Max.
Hydrazine	0.1 ppm Min.

In the case of operating a OTSG in a solid condition, the quality of the feedwater will be low for a period of time after this mode of operation is initiated. The reason is that flooding of the steam generator will result in the dissolution of any tube deposits into the water and subsequent carryover into the external closed cooling loop. With a demineralizer operating to cleanup the external loop and feedwater, the feedwater and steam generator water should reach a condition where the feedwater and steam generator water have the same quality and consequently the same specifications.

5.2.1 pH

The pH must be maintained above 9.3 (9.3-10.5) to prevent low temperature corrosion of the steam generator materials should sulfur compounds and/or oxygen be present. Sulfur compounds in an acid environment could cause tube damage. If oxygen is present, a similar result is possible in addition to the general corrosion of the carbon steel surfaces. The pH is adjusted by the use of ammonia. A pH of 9.3 at 77F is equivalent to an ammonia concentration of 1.5 ppm.

5.2.2 Oxygen

Oxygen is generally an accelerator for corrosion reactions involving carbon steel and inconel surfaces. Since it may be difficult to determine the true extent of chemical contamination of the OTSG's, oxygen control is necessary because the potential for causing local detrimental enviroments by contamination - oxygen interaction. is high.

5.2.3 Hydrazine

Hydrazine should be added to provide a reducing environment and retard of the oxidation of carbon steel. At the temperatures of the feedwater and the water in the OTSGs, little if any oxygen reaction should occur. However, hydrazine is beneficial in maintaining iron oxide films in a protective reduced form.

5.2.4 Cation Conductivity

Cation conductivity is a general measure of the water purity when cationic control additives are present (e.g., ammonia and hydrazine) and thus responds to the presence of anionic contaminants These contaminants could produce a corrosive environment in the OTSG and should be controlled.

5.3 Feedwater With System Isolated in Wet Layup Condition (Condition B)

With the Mini DH system operation, the feedwater system should be layed up (under a nitrogen blanket, if not full) and maintained with water treated with ammonia and hydrazine as follows:

pH at 77F	9.5-10.5
Ammonia	10 ppm initially 2-20 ppm range
Hydrazine	100 ppm initially 50-200 ppm range
Chloride	1 ppm Max.

This chloride specification applies if a stainless steel feedwater heater is layed up.

6. STEAM GENERATOR WATER

6.1 General

As described in Section 5.1. the steam generators can operate in a steaming condition with a vacuum being maintained by a condenser (e.g., main condenser) or in a solid condition with a closed external loop. At other times (e.g., with the mini DH system operating), the units and maintained in wet layup condition.

6.2 Steam Generator Steaming Under a Vacuum

For this condition the OTSG water Specifications are:

pH at 77 F	9.5-10.5
Cation conductivity	10μmho/cm Max.
Chloride	1.0 ppm Max.
Sodium	2.0 ppm Max.

6.2.1 pH

As stated in Section 5.2.1, the OTSG pH must be maintained on the basic side to prevent low temperature corrosion of the steam generator materials should sulfur compounds and/or oxygen be present. This is especially true when steaming in the OTSG results in the concentration of contaminants in the feedwater.

6.2.2 Cation Conductivity

With the presence of ammonia and hydrazine, cation conductivity is the most practical measure of the water quality and the anionic contaminants in the water.

6.2.3 Sodium and Chlorides

Sodium and chlorides are undesirable because they can lead to damage to the steam generators. Also, these two items can be a general indication of the contamination levels in the steam generator water.

6.2.4 Chemistry Control

When out-of-specifications occur in the steam generator, the conditions should be corrected by blowdown or feed and bleed operations.

6.3 Steam Generator Operating With A Solid Condition

The specifications for the steam generator water in this condition is the same as those for the feedwater listed in Section 5.2.

6.4 Steam Generator In An Isolated Wet Layup Condition

When a steam generator is isolated, it is layed up by filling it with water conditioned with ammonia and hydrazine under a nitrogen blanket (if possible) or as follows:

pH at 77 F	9.5 - 10.5
Ammonia	10 ppm initially 2-20 ppm range
Hydrazine	100 ppm initially 50-200 ppm range
Cation conductivity	10 μmho/cm max
Sodium	2 ppm max
Chlorides	1 ppm max

This is basically the same layup chemistry listed in Section 5.3 for the feedwater and the comments listed for the feedwater in that section also apply here for the layup of a steam generator. The additional requirements for limits on sodium and cholorides because of the concern of the effects of these chemicals on steam generator materials.

7. MAKEUP AND FILL WATER FOR STEAM GENERATORS AND FEEDWATER SYSTEMS

Water added to the steam generators or to the feedwater shall meet the following requirements:

Dissolved Oxygen	0.1 ppm max.
Cation Conductivity	1 μmho/cm

Water with low dissolved oxygen levels is desired to limit the contributions from this source to the oxygen in the feedwater and steam generator water, oxygen promotes the general corrosion of steam generator and feedwater system materials: cation conductivity is the measure of the quality of the water. The 1.0 μmho/cm max corresponds to the feedwater specifications when a steam generator is operating.

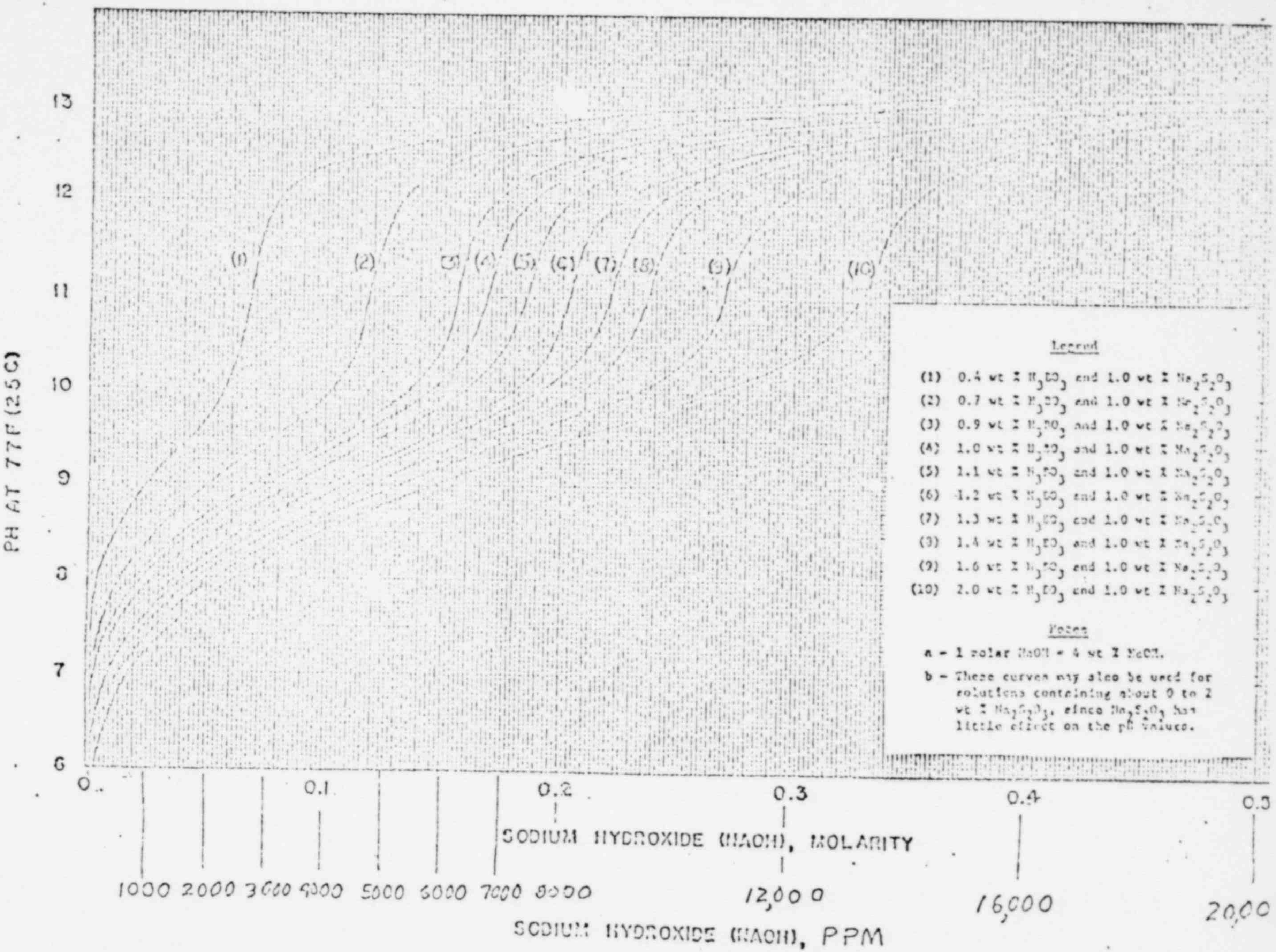

FIGURE 1 PH OF SODIUM THIOSULFATE — BORIC ACID — SODIUM HYDROXIDE SOLUTIONS

REFERENCE: LETTER FROM R.D. SHERRILL TO D.A. NITTI DECEMBER 30, 1975, FILE: 2203.

POOR ORIGINAL