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PROCESS SPECIFICATIONS
REACTOR COOLING WATER TREATMENT

JULY 15, 1953

Classification Cancelled (Change to
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TECHNICAL SECTION
ENGINEERING DEPARTMENT

By Authority of: SE Gydesen 7/15/8
B Roberts 7/15/8

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ENGINEERING DEPARTMENT

Process Specifications

Reactor Cooling Water Treatment

The following specifications have been provided in accordance with the responsi-
tiss established for the Engineering Department by Organization and Policy G.
Number 03.1.2. These Process Specifications define the normal limitations un-
which reactor cooling water is treated for the B, C, D, DR, F, and H reactors.
additional information is obtained, it is intended to review, and if necessary
alter these specifications to conform with this new knowledge. Experimental
tions from these specifications are permitted on the basis of properly appro-
production tests.

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Process Specifications

Reactor Cooling Water Treatment

The following specifications have been provided in accordance with the responsibilities established for the Engineering Department by Organization and Policy Guideline Number 03.1.2. These Process Specifications define the normal limitations under which reactor cooling water is treated for the B, C, D, DR, F, and H reactors. If additional information is obtained, it is intended to review, and if necessary, alter these specifications to conform with this new knowledge. Experimental deviations from these specifications are permitted on the basis of properly approved production tests.

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Under special circumstances, the continuity of production or the attainment of certain objectives of a production test may necessitate temporary relaxation of process specifications. The Manager, Pile Technology is authorized to approve such temporary relaxation of individual specifications, after having discussed the proposed deviation with the Superintendent, Process. These temporary relaxations contemplate periods of time of less than one week and are to be reported in writing by the Manager, Pile Technology to the Manager, Technology and to the Manager, Manufacturing.

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Process Specifications
Reactor Cooling Water Treatment

Page No. 1-1

Date: 7-15-53

Specification: 1.00

Coagulant Addition

References: Kidder, C. P., "CMX Final Report", 7-~~1111~~ (7-31-46).
Water Quality and Treatment, AWWA Manual, 2nd Edition, 1951.
Woods, W. C. A., "Interim Report Number 1, PT-105-503-Z, The Use of
Activated Silica as a Coagulation Aid for Aluminum Sulfate",
HW-27115.
Woods, W. C. A., "Process Water Quality Control with the Alum-Activated
Silica Coagulation Process", HW-28389, June 18, 1953.

Basis:

1.01 The heat generated during reactor operation is removed by pumping water continuously through the reactor. The quality of this water must be controlled to prevent (a) excessive corrosion of the slugs or process tubes, (b) excessive film formation on the slugs and tubes, and (c) excessive effluent water radioactivity.

The quality of the source water from the Columbia River is tabulated below:

SEASONAL VARIATION IN COLUMBIA RIVER WATER

<u>Constituent</u>	<u>Maximum</u>	<u>Minimum</u>
Turbidity	350 ppm	2 ppm
Iron	5 ppm	0.03 ppm
Sulfate	12 ppm	9 ppm
Chlorides	1.2 ppm	0.2 ppm
Hardness	75 ppm	65 ppm
Calcium	24 ppm	18 ppm
Magnesium	5 ppm	4 ppm
Methyl Orange Alkalinity	60 ppm	55 ppm
pH	8.2 ppm	8.0
Manganese	0.2	0.005

The usual concentrations are close to the minimum values except during the period from February through June of each year.

To produce the desired quality of process water, all available information shows that it is primarily necessary to reduce the iron and turbidity without appreciably increasing the hardness of the water. Iron is undesirable because excessive iron concentration in the process water increases the film formation rates. Turbidity is controlled to prevent possible abrasion of process tube and slug surfaces and because high turbidity may also increase film formation. The concentration of manganese,

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which is undesirable because of its high induced radioactivity and 2.6 hour half life, is also reduced by the water treatment process.

Since the impurities in the water exist primarily as colloidal particles with a negative charge, the addition of a multivalent positive ion will neutralize the charge and form a hydrous oxide floc in alkaline water. The gelatinous precipitate, or floc, absorbs and enmeshes the impurities and coalesces into coarser particles which are removed by sedimentation and filtration.

The coagulants, or floc-formers, available for large scale use are limited for economic reasons to a commercial grade salt of aluminum or iron. Process water produced by the correct use of aluminum sulfate or filter alum has been found to give negligible film formation rates in the pile. Generalized corrosion rates obtained under these conditions are lower than with water flocculated with ferric sulfate. In addition, effluent activity levels have been satisfactory. The major advantage of alum over ferric sulfate as a coagulant is that the former makes possible the use of activated silica as a coagulation aid, resulting in filtration rates as high as 4.5 gpm/ft² with the present filter beds. It appears that activated silica is required with alum during periods of low river water temperature or high turbidity conditions to permit filtering rates of 3.0 gpm/sq. ft. or above.

The quantity of coagulant required depends primarily on the kind and amount of impurities in the water and the desired quality of the process water; in addition, it is affected by the water temperature, pH, and to a minor extent by the mixing and settling times before filtration.

The time of mixing following coagulant addition can be divided into two phases. The first is a violent and rapid agitation of the water after coagulant addition to assure uniform distribution of the chemical throughout the water. The second is a longer and gentler mixing, or flocculation, which allows the floc particles to grow in size. These factors are fixed by plant design and flow rate and it is only necessary to add sufficient amounts of coagulant to obtain a satisfactory floc with the fixed time of mixing. After the floc has been formed, it is allowed to settle as much as possible by reducing the velocity of the water. After passing through the sedimentation basins, the water is filtered through rapid sand filters.

The final criteria of the amount of coagulant, and coagulant aid, which must be added are the in-pile effects of the process water. By maintaining the process water quality so that a film formation rate is negligible, it has been found that low aluminum corrosion rates and satisfactory effluent activity levels are obtained. Thus, control of the process water quality from the film formation viewpoint will result in satisfactory overall results in the pile.

Because film formation is a complex phenomenon, it has not been found possible to predict accurately the occurrence of film formation by measurement of process water impurities. Consequently, film formation rates can be most simply controlled by measurement of film formation in the pile. A satisfactory method of film-formation measurement is obtained by application of standard statistical methods to process tube Panellit pressure data, as described in Reference 4. It is thereby possible to define the point at which film formation becomes significant. For the purposes of this specification, a significant film formation rate is defined (in Reference 4)

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that rate which will exceed the control limits corresponding to the particular confidence level chosen. The highest allowable confidence level, corresponding to the broadest control limits, is 99 per cent. Rates of addition of the coagulating chemicals can then be changed as required so that there is normally no significant increase in film formation rates.

1.02 Although film formation and slug corrosion rates are higher when ferric sulfate is used as the coagulating chemical, it is recognized that the B and H reactor areas do not now have facilities necessary for easy and convenient change-over to aluminum sulfate. Ferric sulfate can be substituted in these areas until such a time that the necessary facilities are available. However, the effects of the conjoint use of the two coagulants have not been established.

Specifications:

1.01 Aluminum sulfate (Chemical No. 103, HW-19156) shall be added continuously to the raw water inlet of the Head House as required to maintain the process water quality so that no significant increase in film formation rate takes place in the reactor process tubes. In addition, the process water quality will be maintained at all times within the following limits:

<u>Impurity</u>	<u>Maximum Concentration, ppm</u>
Iron as Fe	0.03
Aluminum as Al	0.50
Turbidity	0.20

1.02 Ferric sulfate (Chemical No. 118, HW-19156) will be added continuously at the raw water inlets of the 183-B and 183-H Head Houses. Sufficient ferric sulfate will be added so that a residual iron concentration of less than 0.05 ppm is maintained in the process water supplied to the B and H reactors. Aluminum sulfate will not be used in conjunction with ferric sulfate.

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Process Specifications
Reactor Cooling Water Treatment

Page No. 2-1

Specification: 2.00

Date: 7-15-53

Activated Silica Addition

References: Woods, W. C. A., "Interim Report Number 1, PT-105-503-E, The Use of Activated Silica as a Coagulation Aid for Aluminum Sulfate", HW-27115.

Basis:

2.01 The use of a coagulation aid has been found to increase the rate of floc formation and to produce a stronger floc with better filtering characteristics. Experimentation demonstrates that activated silica is an effective coagulation aid when used in conjunction with alum coagulant. The use of the coagulant aid results in decreased filter breakthrough tendencies, which in turn enables appreciably increased filtering rates with the process water quality now specified. Since the effectiveness of flocculation with aluminum sulfate decreases rapidly at low water temperatures, the addition of a coagulation aid may be required during the winter to maintain satisfactory filtering rates. Also, it enables high filtering rates to be maintained during the high river water turbidity occurring in the spring. Its use at other times of the year is a matter of economic desirability.

The preparation of activated silica is accomplished by partially neutralizing a sodium silicate solution with dilute sulfuric acid. The degree of neutralization, the silica concentration, and the aging time must be carefully controlled to assure proper floc formation and to prevent gel formation in the mixing equipment.

2.02 The use of activated silica with ferric sulfate has not been demonstrated to produce the improvement in floc formation that has been found with aluminum sulfate.

Specifications:

2.01 The following process will be used to prepare activated silica:

1. Sodium silicate (Chemical No. 113, HW-19156) will be diluted with water to a final concentration of 1.3 - 1.6 per cent SiO_2 by weight.
2. Sufficient diluted sulfuric acid (Chemical No. 116, HW-19156) will be added with agitation, to the sodium silicate solution so that 82 - 85 per cent of the Na_2O content is neutralized. The acid will not be added until the sodium silicate concentration is less than 2.5 per cent SiO_2 by weight.
3. The sulfuric acid will be diluted with water to 10 per cent or less by volume before addition to the silicate solution.
4. The resulting mixture, containing 1.3 - 1.6 per cent SiO_2 by weight and with 82 - 85 per cent of the Na_2O neutralized, will be aged without agitation for a period of at least one (1) hour.

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Page No. 3-1

Date: 7-15-53

Specification: 3.00

Chlorine Addition

References: Kidder, C. P., "CMX Final Report", 7-4444 (7-31-46).
Water Quality and Treatment, AWWA Manual, 2nd Edition, 1951.

Basis:

3.01 Algae are minute forms of plant life which exist in practically all natural surface water and can seriously interfere with the filtration process if allowed to develop unchecked in reservoirs and retention basins. Algae can be controlled by use of algicides. The two most widely used algicides are copper sulfate and chlorine; the latter was chosen to treat process water, as copper would increase both aluminum corrosion and effluent activity.

Chlorine when added to water reacts to form hypochlorous acid which dissociates to form the hypochlorite ion according to the following reactions:



That chlorine existing in water as hypochlorous acid and hypochlorite ion is defined as free available residual chlorine, while that residual chlorine existing in chemical combination with ammonia or organic nitrogen compounds is defined as combined available residual chlorine. For the purposes of this specification, free chlorine is defined as the sum of the free and combined available residual chlorine.

The presence of chloride ions causes increased aluminum corrosion. Experimental evidence shows that by maintaining very low concentrations of chloride and free chlorine, corrosion of aluminum resulting from chloride ion can be minimized.

Specifications:

3.01 Chlorine (Chemical No. 104, HW-19156) shall be added continuously to the inlet of the 182 Buildings or the 183 Buildings raw water flumes. If desired the chlorine may be added simultaneously at both points of addition. Sufficient chlorine will be added so that the free chlorine residual in the 183 Building clearwells is detectable with the approved analytical method (HW-27229). The maximum chloride and free chlorine concentrations in the clearwells will be 2.0 and 0.2 ppm respectively.

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Process Specifications

Reactor Cooling Water Treatment

Specification: 4.00

Page No. 4-1

pH Adjustment

Date: 7-15-53

References: Atwood, J. M., "Process Water pH Effects", HM-24007, 5-15-52.

Basis:

4.01 Process water pH must be carefully controlled because of its effects on iron and aluminum corrosion and film formation rates. Aluminum corrosion, as measured by weight loss, increases with pH in the range 6.0 to 8.0. However, corrosion pitting attack decreases as pH is increased in this range. Since a generalized corrosion attack appears more acceptable than pitting corrosion, pH must be maintained above 7.5. An alkaline pH is more desirable from the standpoint of iron corrosion. Film formation rates increase slightly as pH is lowered in the range 8.0 to 6.0, primarily because of increased iron pickup in the piping system at low pH values. It has been shown that the pH must be below 7.5 for proper coagulation with the alum-activated silica process. The ferric sulfate coagulant can be used with a coagulation pH as high as 7.8.

Raw water pH is quite close to 8.0. Addition of the coagulant lowers this value in proportion to the amount added generally in the range 7.2 to 7.4. To raise pH to the specified value, a base must be added. Choice of the base is primarily one of cost, ease of handling, solubility factors, and effluent activity considerations. The point of addition of the base is determined by the coagulation pH requirements.

Specifications:

4.01 Sufficient hydrated calcium oxide, or lime, (Chemical No. 108, HM-19156) shall be added continuously to the filter effluent water so that the pH of the process water is maintained within the limits of 7.5 - 7.8 measured at the ambient water temperature. When ferric sulfate is used, the lime will be added at the point of coagulant addition so that the process water pH is maintained within 7.5 - 7.8 measured at the ambient water temperature. The lime so added shall be of a form such that 90 per cent by weight of the particles pass through a 100 mesh screen.

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Process Specifications

Reactor Cooling Water Treatment

Specification: 5.00

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Filtration of Process Water

Date: 12-22-53

References: Woods, W. C. A., "Interim Report Number 1, PT-105-503-E, The Use of Activated Silica as a Coagulation for Aluminum Sulfate", HW-27115, April 9, 1953.
Woods, W. C. A., "Interim Report, Pile Technology Development Test 105-524-E, 100 Areas Filter Plant Hydraulic Limit Tests", HW-29778, November 9, 1953.

Basis:

5.01 The materials constituting the filter bed should allow the production of the proper quality and quantity of filtered water without too frequent backwashing of the filter occasioned by either breakthrough of impurities or excessive head loss. The use of the alum-activated silica coagulation process makes possible the production of process water with specified impurity concentrations under practically all conditions affecting the chemical treatment. The problem of impurity breakthrough is thus virtually eliminated, since breakthrough can be controlled by increasing the addition rate of the silica. However, the use of increased amount of activated silica has been found to increase the rate of head loss increase, thereby decreasing the length of filter runs. This problem is further aggravated by increases in the filtration rate. The rate of head loss increase can be decreased by increasing the amount of anthracite in the filter bed and use of the maximum amount of anthracite specified has been found to give satisfactory results with filtration rates up to 5.2 gpm/ft². Any combination of the amounts of filter bed materials defined in Specification 5.01 has been found to give satisfactory impurity concentrations in the filtered water.

5.02 Backwashing of the filters is necessary to remove the impurities which gradually accumulate in them before these impurities unduly restrict water flow through the filter. The backwash water should not contain these impurities.

Specifications:

5.01 The composition of the filtering media in the bed shall be as follows, from bottom to top:

10-14 inches graded gravel of 1 inch maximum size.

3-20 inches graded sand of 0.3 - 0.5 mm effective size

10-27 inches graded anthracite of 0.7 - 0.8 mm effective size

The total depth of the sand and anthracite shall not exceed 30 inches

5.02 Filtered water shall be used for filter backwash water.

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PRODUCTION ENGINEERING DEPARTMENT
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Process Specifications

Reactor Cooling Water Treatment

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Date: 7-15-53

Specification: 5.00

Filtration of Process Water

References:

Basis:

5.01 The materials constituting the filter bed should allow the production of the proper quality and quantity of filtered water without too frequent backwashing of the filter caused by either breakthrough of impurities or excessive head loss. The use of the filtration materials specified below has been demonstrated to yield satisfactorily low concentrations of undesirable impurities such as aluminum, turbidity, iron, and manganese.

The total depth of the filter bed is determined by the filter construction. The filters were designed for a flow rate of 2.6 gpm/sq. ft. but it has been found possible to operate them at a rate of 4.5 gpm/sq. ft. with the alum-activated silica treatment process.

5.02 Backwashing of the filters is necessary in order to remove the impurities which gradually accumulate in them before these impurities unduly restrict water flow through the filter, or before the impurities pass through the filter. The backwash water should not contain these impurities.

Specifications:

5.01 The filter layers from bottom to top of the filtering media in the bed shall have the following composition:

- 10-14 inches graded gravel of 1 inch maximum size
 - 10-20 inches graded sand of 0.3 - 0.5 mm effective size
 - 10-20 inches graded anthracite of 0.7 - 0.8 mm effective size
- The total depth of the sand and anthracite shall not exceed 30 inches

5.02 Filtered water shall be used for filter backwash water.

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Process Specifications

Reactor Cooling Water Treatment

Specification: 6.00

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Sodium Dichromate Addition

Date: 7-15-53

References: Lutton, J. M. "Sodium Dichromate as a Process Water Additive: An Evaluation," HW-27158, March 19, 1953.
Shields, R. J., "Interim Report, Production Test Numbers 105-9-P, 105-103-P, 105-362-P, 105-460-P, Corrosion of Slugs," HW-24134, April 18, 1953.
Greninger, A. B. to Gross, C. N., "Interim Process Specification - Sodium Dichromate Addition to 100 Areas Process Water," HW-27679, April 8, 1953.

Basis:

.01 Corrosion of the slugs and tubes in the reactors must be carefully controlled in order to prevent the occurrence of ruptured slugs and tube leaks, resulting from corrosive attack by the reactor cooling water. This attack is characterized by the removal of aluminum from the entire metal surface at a definite, uniform rate. Superimposed on this uniform rate of corrosion may be a localized attack in which small areas of the surface are penetrated at a much greater rate. This latter type of attack will lead to more serious consequences to the efficiency of reactor operations. Penetration of process tubing will result in water leaking into the graphite moderator, causing reactivity losses and increased corrosion problems. This latter problem arises from the graphite-aluminum galvanic cell which is set up in the presence of water. In this couple, the aluminum will corrode, resulting in additional leaks. Penetration of the aluminum cans of the slugs can result in an increased rupture rate. These deleterious effects are caused by erratic and unpredictable variations in process conditions, such as misaligned slugs, water quality changes, or local galvanic cells.

The severity and frequency of the local attack can be greatly reduced by the addition of a corrosion inhibitor. Reactor operation without the addition of a corrosion inhibitor was characterized by increased pitting attack on the unloaded sections of process tubes, partial removal of the protective 72-S cladding in the downstream portion of the tubes, and severely pitted slugs and tubes. Of the commercially available inhibitors, only sodium dichromate has been used extensively under reactor operating conditions. A critical review of the effects of dichromate ion has concluded that 2 ppm of sodium dichromate will definitely inhibit these phenomena. It is further concluded that the instantaneous concentration of the sodium dichromate required for adequate protection can vary by at least ± 1 ppm from the above value. Since experience has also shown that the uniform rate of aluminum corrosion in the presence of 2 ppm of sodium dichromate is satisfactory for successful operation of the reactors, the use of dichromate is desirable for control of slug and tube corrosion.

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Specifications:

6.01 Sodium dichromate (Chemical No. 112, HW-19156) shall be added continuously to the reactor cooling water after the coagulation and filtration treatment. Sufficient sodium dichromate will be added so that the instantaneous concentration is 2.0 ± 1.0 ppm and the daily average concentration is 2.0 ± 0.2 ppm as $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.

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Process Specifications
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Specification: 7.00

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Purge Material Addition

Date: 7-15-53

References: Conley, W. R., "Final Report - Production Test 105-3-MR, The Use of Dicalite Diatomaceous Earth as a Purge Material in the 100 Areas", HW-24560, May 26, 1953.
Wilson, C.D., "Flow Laboratory Investigations of 'F-Type' Pitting of Slugs and Tubes", HW-28207, July 1, 1953.

Basis:

7.01 Film formation on slug and tube surfaces causes a decrease in water flow rates and lowers the heat transfer coefficient from slug to water, which increases both tube and slug surface temperature. Both of these effects tend to increase slug corrosion rates. The quantitative effect of film on slug corrosion is not known, but it is believed that increased amounts of film will increase slug corrosion rates. For this reason film is periodically removed from the tube and slug surfaces.

Methods of removing film tested in the laboratory indicated that the film could be removed with either oxalic acid or a Johns-Manville diatomaceous earth slurry. Later in-pile tests indicated that the oxalic acid method was unsatisfactory. The only alternative forms of diatomaceous earth investigated in pile tests have been Dicalite #4200 and Dicalite Special Speed Flow. Continuous addition of the purge material while the reactor is operating may result in serious abrasion of the slug and tube surfaces. Sodium dichromate may not inhibit this attack with the high concentrations of purge material required. Consequently, it is necessary to restrict the period of time in which purge material may be added to avoid excessive attack on the slugs and tubes, which could lead to ruptured slugs and penetration of the tubes. The extent of any such attack is apparently dependent on the product of the solids concentration and the length of time in which the solids are added.

A more complete discussion of the effects of film, its measurement, and the allowable amount of film is contained in the specifications for the Reactor (Pile) Process.

Specifications:

7.01 When required for the removal of film, purging shall be done by adding Johns-Manville Standard Super-Cel or equivalent to the process water at a concentration of not over 150 ppm. The purging shall be conducted so that there are no more than 300 ppm-hours in any consecutive thirty day period.

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Process Specifications

Reactor Cooling Water Treatment

Specification: 8.00

Page No. 8-1

Emergency Water Treatment

Date: 7-15-53

References:

Basis:

8.01 The assured supply of cooling water to a reactor is very important as the slug jackets and the process tubes would quickly melt if the water supply to a tube were interrupted during pile operation. Even after a reactor is shutdown, the process metal continues to liberate heat from beta and gamma radiation and this heat must be removed to prevent the slugs and tubes from reaching excessive temperatures. Normally several hours supply of process water is available in storage tanks. Filtered water is also held in elevated tanks for immediate use in case of emergency. In addition to the above storage facilities, the Reactor Areas are supplied with inter-connecting lines to supply raw water to any Reactor Area in emergency. It is anticipated that raw water will be used for cooling only in the event of total failure of the treated water supply or complete evacuation of an area.

Specifications:

8.01 When a reactor is shut down, filtered water may be used for emergency cooling. In the event of failure of the treated water supply facilities, raw water may be used for reactor cooling.

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Process Specifications

Reactor Cooling Water Treatment

Specification: 9.00

Page No. 9-1

Restriction on Chemical Additives to Process Water

Date: 7-15-53

References: HW-19156, "Specifications, Acceptance and Sampling Procedures for Essential Materials."

Basis:

9.01 It has been found that very small concentrations of various chemical elements, such as trivalent chromium, copper, manganese, iron, lead, mercury, or boron, in the reactor process water can have a significant effect on aluminum corrosion, film formation, pile reactivity, and effluent water activity. Commercially available chemicals may contain these elements either as major constituents or as trace impurities. Thus, the effect of the addition of chemicals other than those specified to the process water must be carefully investigated before their use can be allowed.

Specification:

9.01 No other materials except those specified below shall be added to the reactor process water. These chemicals shall be as described in the reference document and shall be added only as described in the foregoing specifications.

<u>Name</u>	<u>Chemical Number</u>
Ferric Sulfate	118
Aluminum Sulfate	103
Sodium Silicate	113
Sulfuric Acid	116
Chlorine	104
Lime	108
Sodium Dichromate	112
Diatomaceous Earth	Johns-Manville Standard Super-Cel or Equivalent

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ENGINEERING DEPARTMENT

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Process Specifications

Reactor Cooling Water Treatment

The following specifications have been provided in accordance with the responsibilities established for the Engineering Department by Organization and Policy Guideline Number 03.1.2. These Process Specifications define the normal limitations under which reactor cooling water is treated for the B, C, D, DR, F, and H reactors; additional information is obtained, it is intended to review, and if necessary, alter these specifications to conform with this new knowledge. Experimental deviations from these specifications are permitted on the basis of properly approved production tests.

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Date 12/1

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