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ADDITION OF SOLUBLE AND INSOLUBLE NEUTRON ABSORBERS TO THE REACTOR COOLANT SYSTEM OF TMI-2

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ABSTRACT

The physical and chemical properties of six elements were studied and combined with cost estimates to determine the feasibility of adding them to the TMI-2 reactor coolant to depress k_{eff} to less than or equal to 0.95. Both soluble and insoluble forms of the elements B, Cd, Gd, Li, Sm, and Eu were examined. Criticality calculations were performed by Oak Ridge National Laboratory to determine the absorber concentration required to meet the 0.95 k_{eff} criterion. The conclusion reached is that all elements with the exception of boron have overriding disadvantages which preclude their use in this reactor. Solubility experiments in the reactor coolant show that boron solubility is the same as that of boron in pure aqueous solutions of sodium hydroxide and boric acid; consequently, solubility is not a limiting factor in reaching the k_{eff} criterion. Examination of the effect of pH on sodium requirements and costs for processing to remove radionuclides revealed a sharp dependence; small decreases in pH lead to a large decrease in both sodium requirements and processing costs. Boron addition to meet any contemplated reactor safety requirements can be accomplished with existing equipment; however, this addition must be made with the reactor coolant system filled and pressurized to ensure uniform boron concentration.

FOREWORD

At the time the study was begun, the shutdown margin provided by the existing boron concentration was a subject of debate due to assumptions made relative to the extent of core damage and the present core configuration. This led to discussions of the shutdown margin and the required boron concentration corresponding to that margin for other fuel configurations which might arise during defueling operations. This study was undertaken to examine the feasibility of adding more neutron absorber (boron or suitable alternatives) to the reactor coolant system, thereby increasing the shutdown margin to the extent that a criticality accident would be incredible regardless of the configuration of the fuel.

In order to evaluate the feasibility of the absorber addition, the shutdown margin that would render a criticality accident incredible had to be defined and the corresponding concentration of absorber quantified. For the purposes of this study only, we established the criterion that a criticality event would be incredible when $k_{eff} \leq 0.95$ with the fuel in a highly reactive configuration but suitably "poisoned" by added soluble or insoluble neutron absorbers. A conservative model of the reactor was developed to serve as the foundation for calculations to determine the absorber concentrations required to meet the reactivity criterion. Both the model and the criterion were formulated based on the advice of reactor physics consultants. Oak Ridge National Laboratory performed the calculations.

Because the actual concentration of absorber was not available until late in the study schedule, a range of poison concentrations was considered in making chemical, economic and engineering evaluations. The results provide a useful basis for management decisions for specification of the appropriate margin of subcriticality. It must be emphasized that the poison concentration used for purposes of comparative evaluations, 5500 ppm boron equivalent, is not intended to serve as a recommended value.

An increase in the boron concentration requires that the primary coolant system be treated by bleed/feed methods until the average boron concentration reaches the new specification. This condition may be insufficient to prevent criticality accidents arising from local boron concentrations lower than the mean value; thus, complete mixing, designed to produce a homogeneous boron concentration, is also required. With the reactor coolant system (RCS) in a partially drained condition, communication between the primary coolant in the reactor vessel and in the cold leg piping is poor at best. If the RCS were pressurized and refilled, the time required for almost complete mixing of the primary system is less than one week.

The decision has been made recently to increase the boron concentration to almost 4,500 ppm (the upper Technical Specification) while refilling and repressurizing the RCS. Also, a Technical Specification change has been requested to increase the upper limit for boron concentration to 6000 ppm, which is anticipated to be well above any concentration required to assure an adequate shutdown margin during defueling operations. The administrative choice of a new lower Technical Specification limit and the operating concentration somewhat above that limit is expected in the near future.

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ADDITION OF SOLUBLE AND INSOLUBLE NEUTRON ADSORBERS TO THE REACTOR COOLANT SYSTEM OF TMI-2

1.0 OBJECTIVES AND SCOPE

The purpose of this study is to investigate the feasibility of increasing the macroscopic cross section for neutron absorption by the addition of a poison (soluble or insoluble) to the reactor coolant system (RCS) to the point where a criticality event during fuel removal operations would be incredible.

Absorbers containing the following elements were examined: fully enriched boron,[a] cadmium (Cd), europium (Eu), gadolinium (Gd), lithium (Li), and samarium (Sm). The soluble forms of the poisons studied were boron and fully enriched boron as borates and the other elements in the form of nitrates or sulfates. Insoluble absorbers include alloys, glasses, or ceramics containing a relatively high volume concentration of one of these elements. Evaluations of the physical and chemical properties of the poisons are presented in Chapter 2.

In order to evaluate the feasability of the absorber addition, the shutdown margin that would render a criticality accident incredible had to be defined and the corresponding concentration of absorber quantified. For the purposes of this study only, the criterion was established that a criticality event would be incredible when $k_{eff} \leq 0.95$ with the fuel in a highly reactive configuration but suitably "poisoned" by added soluble or insoluble neutron absorbers. A conservative model of the reactor was developed to serve as the foundation for calculations of the absorber concentrations required to meet the reactivity criterion. Both the model and the criterion were formulated based on the advice of reactor physics consultants. Oak Ridge National Laboratory (ORNL) performed the calculations to determine the maximum reactivity of the model at various poison concentrations. The model, analytical method, and results are presented in Chapter 3.

After evaluation of the physical and chemical properties of the potential poisons in terms of the current requirements at TMI-2, the optimum poison remains boron in the form of boric acid. There is no reasonable alternative because of the chemical compatibility problems, the unacceptably long time required for comprehensive development and testing of a compatible alternative, and the cost advantages boron maintains over its competitors. A method of deriving the correct concentration, adding it to the RCS and monitoring the concentrations is the subject of Chapter 4. Chapter 5 deals with the economics of increasing the concentration to the k_{eff} criterion, as well as some other concentrations. The economic factors involved in a selection of boron or enriched boron are discussed. Finally, a summary of the major conclusions and recommendations is presented in Chapter 6.

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a. For this study, "fully enriched" boron is used to denote 100% ^{10}B, which is the isotope of boron having favorable neutron absorption properties. The terms "boron", "borates", and "boric acid" without any qualification are used to denote species containing the natural isotopic distribution, which is 19.8% ^{10}B and 80.2% ^{11}B. In those cases where a partial enrichment of ^{10}B is discussed, the percentage of the ^{10}B isotope is given.

2.0 EVALUATION OF PHYSICAL AND CHEMICAL PROPERTIES

This chapter features a compilation and evaluation of poison properties of interest with emphasis on chemical behavior. Replacement or addition of soluble absorbers to the RCS at TMI must be accomplished by bleed-and-feed methods, thereby imposing rigid requirements of physicochemical compatibility on any proposed alternate. The chapter opens with a summary of the current conditions and specifications of the RCS (2.1) as well as a description of the interfacing systems which impose restrictions on coolant chemistry. It is followed by a comparison of pertinent properties of alternate poisons (2.2). A summary of the principal findings of the physicochemical evaluations is presented in Section 2.3. They lead to the conclusion that there is no reasonable alternative to boron or enriched boron. Recent measurements of the solubility of borates in the RCS are presented and compared with published solubility data in pure water (2.4). We examined the specifications of the RCS to determine whether they might be safely revised to accommodate some of the alternate poisons. While this objective was not realized, the study led to some useful conclusions based on the sensitivity of processing costs to pH (2.5).

2.1 Current Conditions and Specifications of the Reactor Coolant System

2.1.1 Chemical Specifications

The RCS is, for all practical purposes, a mildly alkaline, aqueous solution of a combination of H_3BO_3 and NaOH. The Technical Specifications require that pH $\geq$ 7.5 (measured at 77°F) and that the boron content exceed 3000 ppm.[1] In actual practice, the pH is maintained close to 7.8, the boron concentration is 3800 ppm and the sodium concentration is 1100 ppm.[2,3,4] The concentration of other dissolved substances from fuel, fission products, structural materials, air, etc. is insignificant in terms of most, but not all, chemical problems. Small concentrations of ions with redox properties can influence the radiation chemistry. Other solutes, such as oxygen and chloride ion, can play a major role in corrosion. While the Technical Specification for chloride is < 5.0 ppm,[1] the actual value is around 1 ppm.[2,3] The major source of chloride contamination is the NaOH required to maintain the pH specification.

Although the O_2 concentration was low (0.25 ppm) during the four years following the accident,[4] it is approaching the saturation level (8.0 ppm) in the reactor vessel now that the reactor coolant is continuously exposed to air.[5] Also, previous measurements as well as those performed in the course of the study demonstrate that the concentration of extraneous anions, particularly the oxyanions of carbon, sulfur, and nitrogen are low. However, as contact with air increases, the concentrations of carbonates and the dissolved nitrogen will increase.

The temperature of the RCS remains 25 to 30°F above the ambient conditions in the containment, which ranges from 50°F (10°C) in the winter to 80°F (27°C) in the summer.

2.1.2 Interfacing Systems

A change to RCS chemistry may have an effect on interfacing plant systems. According to current defueling plans, the interfacing systems are:

- Defueling Equipment
- Submerged Demineralizer System (SDS)
- EPICOR-II™ System
- Defueling Water Cleanup System (DWC).

For the most part, the defueling equipment is constructed of the same materials as the RCS; it will not be affected by substantial changes in either boron concentration or pH. The processing systems, however, contain organic and inorganic ion exchange media. Their performance is relatively sensitive to increases in the RCS sodium concentration.

The SDS and DWC both contain inorganic zeolites. Their purpose is to maintain a reduced level of gross radionuclides in the RCS and fuel pools during fuel removal. The SDS system has been in routine use since August of 1981 to process reactor building sump water and reactor coolant. Water with boron concentrations approaching 4000 ppm has been successfully processed through the SDS with no significant effect on the zeolites. This is not surprising because these inorganic demineralizers are cation exchangers; thus, even a 100% increase in boron is highly unlikely to directly affect the efficiency of the SDS or increase beyond a negligible level the tendency of the zeolites to remove boron from the coolant. However, the increase in sodium required to maintain the current pH at higher boron concentrations decreases the capacity of the zeolites for cesium.[6] The result is an increased number of liners required for processing and thus, an increase in processing costs.

EPICOR-II™ is an organic, mixed bed, ion exchange system. It is used primarily for antimony removal and as a polishing system prior to storing water in the processed water storage tanks. Past experience shows that boron does not significantly affect resin performance; however, resins absorb residual cations following SDS treatment and the borate anions as well. Saturation with boron occurs after a few thousand gallons are processed, but this imposes no practical limitations. More important is the fact that, as with SDS, the increased sodium concentration required to maintain the pH decreases the capacity of the EPICOR™ liner for cesium.

2.2 Suitability and Compatibility

The suitability and compatibility of potential absorbers were evaluated on the basis of neutronic, physical, and chemical properties.

2.2.1 Neutron Absorption and Solubility

The principal requirement of a potential additive is a large neutron absorption cross section. Table 1 compares the thermal neutron microscopic absorption cross sections of the neutron poisons under consideration and their concentration equivalents to 5500 ppm boron. As shown in Chapter 3, 5,500 ppm boron meets the k_{eff} criterion as applied to the conservative model which serves as the basis for the criticality calculations. The concentration equivalent to 5500 ppm boron depends upon molecular weight as well as thermal neutron cross section[a]. For preliminary screening the concentration equivalence calculations are based on the assumption that the neutron absorption reactions follow purely 1/v behavior.[b]

TABLE 1. RELATIVE NEUTRON ABSORPTION OF VARIOUS SUBSTANCES

Substance	Atomic Weight	σ_{th} (barns)[b]	ppm Equivalent[a] to 5500 ppm B	Equivalence to B by Weight
B	10.8	760	5,500	1
^{10}B	10.0	3,837	1,010	0.166
Gd	157	49,000	1,240	0.225
Cd	112	2,450	17,690	3.23
Sm	150	5,600	10,370	1.89
Eu	152	4,600	12,790	2.33
Li	6.9	71	37,560	6.83

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a. Method of Equivalent Determination

The basic equation is:

$$\frac{\sigma_{th} \cdot N_A \cdot C \cdot \rho}{A} = P$$

where

σ_{th} = thermal neutron absorption cross section, barns/atom

N_A = Avogadro's number, atoms/g-mole

C = concentration, ppm or g elemental poison per 10^6g solution

A = atomic weight, g/g-mole

ρ = solution density, assumed to be 1 g/cm^3

P = poison effectiveness, barns/ml of solution.

Since $P_B = P_x$, equivalence of element x for 5500 ppm boron in fourth column is given by

$$\frac{5500\ \sigma_{th,B} \cdot A_x}{\sigma_{th,x} \cdot A_B} = C_x(\text{ppm}).$$

The fifth column is C_x as calculated in the fourth column divided by 5500.

b. Information in this column is from Reference 8.

A principal concern is the concentration of absorber that can be achieved. For solubles, this is determined by the solubility limits listed in Table 2. Also shown in that table is the concentration required to achieve the k_{eff} criterion in 914,000 gal[c] of unborated water and the fraction of the solubility limit that concentration represents. It should be noted that the solubilities presented in Table 2 are for pure water. The solubility of the chemical compound in the reactor coolant, which has a more complex solution chemistry, may differ from that listed; therefore, the data presented should be taken only as an indication of the solubility in the reactor coolant without accounting for the complications associated with pH, for example. (For a more detailed discussion of boron solubility in the reactor coolant, see Section 2.4.) For insolubles, the concentration of absorber that can be achieved in a given volume depends on the composition of the substance and the packing factor characteristic of the shape of the substance. Another requirement is that the thickness of absorber be less than the mean free path for absorption of thermal neutrons; greater thicknesses are largely ineffective except insofar as they displace moderator.

2.2.2 Chemical Properties and Compatibility

Compatibility with the existing reactor coolant chemistry is a necessary condition for a potential absorber. No matter what system is devised for the introduction of the absorber, there will be a significant residue of the present reactor coolant with which the new absorber would come into contact; no poison precipitation reactions can be tolerated as a consequence of the mixing of the two media. In addition to ordinary chemical compatibility, the absorber must be able to withstand radiation fields up to 5 krad/h for at least two years. Still further, an alternate poison system must not lead to intolerable corrosion problems nor interfere with the ion exchange removal of the fission products.

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a. See Table 1, footnote a.

b. On the basis of this assumption, Table 1 shows that one unit weight of Gd is equivalent to four units of B. More detailed calculations[7] indicate that the equivalence ratio is closer to 1:3 at $k_{eff} \approx 0.95$.

c. 914,000 gal is the estimated maximum volume of water required for defueling, which assumes that the refueling canal is filled.

TABLE 2. SOLUBILITIES OF VARIOUS ABSORBERS

Compound	Solubility[a] (mg/l x 10^{-3})	Concentration Required[b]	
		(mg/l)[c]	% Solubility[d]
$Cd(NO_3)_2$	1100 (0°)[e]	37,200	3.4
	3260 (60°)	------[f]	1.1
$Cd(NO_3)_2.4H_2O$	2150 (0°)	48,500	2.2
$CdSO_4$	770 (0°)	32,800	4.3
	610 (10°)	------[f]	5.4
$3CdSO_4.8H_2O$	1140 (0°)	40,400	3.5
	1280 (60°)	-------[f]	3.2
$Gd_2(SO_4)_2.8H_2O$	30 (25°)	2,950	9.8
$Gd(NO_3)_2.6H_2O$	1440 (25°)	3,560	0.2
$LiNO_3$	530 (0°)	373,000	70
	1940 (70°)	-------[f]	19
$LiNO_3.3H_2O$	1510 (25°)	666,000	44
$Li_2SO_4.H_2O$	400 (25°)	346,000	86
Li_2SO_4	350 (0°)	298,000	85
	300 (100°)	-------[f]	99
(20% ^{10}B)	35 (10°)	31,400	90
H_3BO_3 (80% ^{10}B)	35 (10°)	5,770	16

Footnotes:

a. Information found in this column is taken from References 9 and 10.

b. Concentration of compound equivalent in neutron absorption to 5500 ppm boron. (See Table 1 for concentration equivalents of elemental absorbers.)

c. This is equivalent to ppm (mg per kg of solution) only for relatively dilute solutions where the specific gravity is approximately unity. For many saturated solutions, and for all solutions of Li under consideration, the specific gravity is substantially greater than unity and the equivalence of mg/l to ppm fails. For $LiNO_3$ at 25°C, the specific gravity of the saturated solution is 1.34 g/cm^3.

d. Concentration required divided by solubility.

e. Temperature in degrees Celcius.

f. Concentration required is independent of temperature.

The compatibility of boron or fully enriched boron has been demonstrated by its current use in the RCS. The isotopic distribution of the boron makes no difference to its chemistry, but increasing the concentration increases the sodium hydroxide required to control the pH, thus increasing the processing costs. Since less fully enriched boron is required to achieve the same neutron absorption as boron (642 ppm ^{10}B[a] per 3500 ppm boron), the effect of its addition to the RCS on processing costs is less than that of a neutronically equivalent addition of boron.

Gadolinium nitrate and sulfate are compatible with the existing reactor coolant chemistry and physical environment in some respects. In its net effect the trivalent gadolinium ion is almost completely inert insofar as its radiation chemistry is concerned. Gd^{+3} is the only stable form in solution. All reviewed electrochemical information indicates it is inert to the fuel cladding, stainless steel and inconel.[11] The trivalent gadolinium ion must be used at pH less than 6.0; at pH greater than 6.0 the gelatinous hydrous oxide begins to precipitate.

The sulfate ion is inert in its radiation chemistry at pH less than 6.0. The authors have found no reasonable route to its conversion to reduced forms in concentrations that could lead to corrosion problems; nevertheless, concern about the use of sulfates persists. It is argued that because the sulfate is potentially reducible (through bacteriological action, for example) to species such as thiosulfate, the attendant long-term corrosion problems preclude its use. The nitrate ion enhances the protection of the structural materials of the primary system to pit corrosion and stress cracking corrosion.[12] On the other hand, it is subject to rapid radiation-induced redox reactions, but this is not likely to be a significant problem. More significantly, nitrate saturation of the EPICOR™ ion exchange resins requires modification of the RCS demineralizer system to prevent rapid uncontrolled oxidation, e.g., a fire.[13] Another demineralizer problem common to all cationic poisons is the competition they offer to fission products for sites on the ion exchangers.

Because the compatibility of gadolinium nitrate or sulfate hinges on a pH below 6.0, the feasibility of maintaining the pH of the reactor coolant below that level must be addressed. If the current criterion for pH > 7.5 is inflexible, it would render impossible the replacement of the current reactor coolant by a bleed/feed method.

The use of gadolinium as a neutron absorber for TMI-2 would still be possible if it were used in conjunction with a complexing agent. A brief search was conducted for a complexing agent for gadolinium that is soluble in water at a pH of about 7.5, withstands the ionizing radiation doses involved, does not harm the zeolite demineralizers, and does not contain components such as halogens that could cause corrosion problems if cleaved from the agent through hydrolysis or radiolysis. Even though the criteria are numerous, so are the number and variety of complexing agents available. Although it may be possible to find a complexing agent that meets these criteria, the search was halted because of the radwaste problems associated with complexing agents. Because of the possibility of relatively rapid migration of chelated radioactive metals, the amount of complexing agents permitted in waste packages is strictly limited.[14]

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a. Fully enriched boron.

The nitrate and sulfate salts of samarium and europium have chemical properties similar, but inferior, to those of the identical compounds of gadolinium.

The electrochemical behavior of the bivalent ion of cadmium is similar to that of the bivalent ion of iron. It is more reactive than the trivalent ion of gadolinium and has a slight tendency to deposit on the structural materials of the primary system at pH greater than 6. Experimental evidence indicates that the rate of deposition is so slow as to present no prohibition to its use as a soluble poison.[15] As for ionizing radiation, it causes no net effect on the Cd^{+2}. More troublesome is the fact that the carbonate is likely to precipitate in the air-saturated alkaline medium. The hydrous oxide is also likely to precipitate at pH $\geq$ 7.7. Another shortcoming is the relatively high concentration required along with concomitant problems of reduced fission product removal by ion exchange.

The monovalent ion of lithium is inert in both the presence and absence of radiation. The solubility data indicate that the concentration of lithium compounds required to meet the k_{eff} criterion is achievable, although that concentration for some compounds may be unacceptably close to the solubility limit. The Li^+ is compatible with the RCS insofar as pH and CO_2 saturation are concerned (i.e., there is no precipitation of hydroxide or carbonate); however, there may be some problem of precipitation of borates during the bleed/feed operation. Another negative aspect that may be cited is the fact that the product of neutron capture by ^6Li is the undesirable tritium nuclide; however, the rate of this nuclear reaction is trivial even at the high concentrations required to meet the k_{eff} criterion. The nitrate loading on the organic demineralizer and the reduction in fission product removal are more substantial problems. Also related costs are quite high.

Several insoluble poisons were considered. Only those containing boron were deemed worthy of further study. Boron carbide (B_4C), either pure or in alumina matrices, meets the chemical and physical compatibility requirements. It is insoluble in water, resistant to acids and oxidation at temperatures up to at least 1500°F. Boron carbide can withstand the high radiation field without adverse effects as demonstrated by the fact that it is commonly used in control rods. The compressive strength of both the pure B_4C and the B_4C/alumina is between 35,000 and 45,000 psi. In addition, they are not so brittle as to present a handling problem.

Borosilicate glass is available in the form of thin-walled, hollow cylinders called Raschig rings. The glass contains 12 wt.% boric oxide which is equivalent to 3.7 wt.% boron. The Raschig rings can be manufactured to ANS standard ANSI/ANS 8.5 - 1979. They are chemically and radiolytically inert; however, the mechanical properties are such that they can break and cause handling problems.

2.2.3 Effects on the Demineralizers

The primary means by which soluble fission products are removed from the reactor coolant are ion exchange media. The media to be used in the defueling water clean-up system are LINDE IONSIV IE-95™ and LINDE IONSIV A-50™, both of which are zeolites. Conditions are such that both the borate and Na^+ concentrations are not affected by the zeolites, while the principal cationic fission products, especially the cesium isotopes, are effectively removed. The selectivity coefficient, which represents the relative affinity of the zeolite for two competing cations, is a function of their charges and diameters. In general, higher affinity is associated with higher charge and greater radius:

$La^{+3} \approx Sm^{+3} \approx Eu^{+3} \approx Gd^{+3} > Cd^{+2} > Cs^{+} > Na^{+} > Li^{+}$ (Reference 6).

The size of the pore openings is also of major importance. Ions with diameters greater than the openings are effectively excluded.

The use of Gd^{+3} as a soluble poison would require a zeolite with a pore size smaller than the diameter of the poison yet large enough to pick up Cs^+ and Sr^{+2}. Currently no data are available to confirm whether this is feasible, especially with the zeolites now in place.

For the Li^+ system (approximately 8 molar), the reverse is the case. The zeolite should have a much higher affinity for low concentrations (micromolar) of fission products than for the soluble poison. Again, no data are currently available to evaluate the feasibility but preliminary investigations are encouraging. Another potential problem cited earlier, particularly with Li^+, is the large nitrate concentration involved and the related possibility of a fire in the organic demineralizer. Similar hazards are associated with the nitrates of the rare earths and Cd.

2.2.4 Insoluble Absorbers and Fuel Removal

The survivability of insoluble absorbers will be most affected by the currently planned fuel removal technique: hydrocyclone vacuuming. In the application of this technique the absorber may be removed with the fuel causing a local poison deficit. This could be serious from a criticality standpoint because the remaining fuel may not have sufficient absorber to maintain the system in a subcritical condition. Also, required replacement of absorber removed with the fuel increases material costs and the fuel canister/shipping costs associated with the increased volume of debris.

2.2.5 Cost and Availability of Alternate Poisons

The total cost of soluble absorbers is dependent on the volume of water in contact with the reactor coolant during defueling operations. Current plans for defueling operations have the reactor coolant in contact with the reactor building fuel canal, the spent fuel canal, the reactor coolant bleed tanks A and C in addition to some other tanks. The combined volume of approximately 914,000 gallons is the basis of the materials cost estimates in Table 3. No credit has been taken for boron currently in the reactor coolant system. If the volume of water used for defueling operations were to be reduced by isolating the RCS from some of the other water volumes, the total cost would be reduced accordingly.

TABLE 3. COST AND AVAILABILITY OF SOLUBLE ABSORBERS

Substance	Amount Required[a] (kg)	Cost ($/kg)	Total Cost[b] ($)	Availability
H_3BO_3 (20% ^{10}B)	1.1×10^5	6.6	730,000	Readily Available.
H_3BO_3 (80% ^{10}B)	2.8×10^4	684	19,000,000	6 month lead time to provide required quantities.
$Cd(NO_3)_2.4H_2O$	9.4×10^3	12	110,000	Readily available.
$3CdSO_4.8H_2O$	7.7×10^3	33	250,000	
$Eu(NO_3)_3.6H_2O$	7.2×10^4	1200	86,000,000	Not readily available in quantities required.
$Eu(SO_4)_3.8H_2O$	5.9×10^4	1400	83,000,000	
$Gd(NO_3)_3.6H_2O$	6.8×10^3	43	290,000	6 month lead time to provide required quantities.
$Gd_2(SO_4)_3.8H_2O$	5.6×10^3	---	-------	
$LiNO_3$	7.1×10^5	6.5	4,600,000	Readily available.
$Li_2SO_4.H_2O$	6.6×10^5	5.5	3,600,000	
$Sm(NO_3)_3.6H_2O$	5.8×10^4	85	4,900,000	Not readily available in quantities required.
$Sm_2(SO_4)_3.8H_2O$	4.8×10^4	100	4,800,000	

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a. Amount required is based on 5500 ppm boron (natural isotopic distribution), the mass equivalents presented in Table 1 and 914,000 gallons of water to be poisoned.

b. Total Cost is the materials cost only and does not include additional processing costs. Processing costs may be significant.

The "total" costs presented on Table 3 are initial materials costs only; they do not include the costs of replacement of absorbers lost in processing, etc., or and the costs of shipping from the chemical plant to Three Mile Island. In most cases, vendors propose to ship the chemicals in the form of a "wet cake" which would have to be made into solution on site at additional man-power costs.

The total cost of europium, around $100 million, is so great that it was dropped from further consideration on these grounds alone. Also highly enriched ^{10}B poses formidable cost problems. Lithium nitrate is also relatively costly. From the same viewpoint, gadolinium nitrate is especially attractive and cadmium nitrate is also worthy of interest.

Table 4 shows the cost and availability of insoluble absorbers. An arbitrarily chosen volume of 2000 cubic feet, which is approximately half the volume of the reactor vessel, was used with a 60% packing factor to calculate the amount required. Pure boron carbide is relatively expensive compared to other insoluble materials and, at the assumed packing factor, the mean concentration of boron is greater than 5500 ppm.

2.3 Principal Findings of Physicochemical Investigations

For soluble absorbers, the obvious choice from a suitability, compatibility, and survivability standpoint is boron or some fractional enrichment of boron. As demonstrated in Chapter 5 and shown in Table 3, enriched boron is far more expensive than boron. The latter has proved to be satisfactory through use and its impact on current systems is known. Its continued use, albeit in increased concentration and under some modified conditions, would require the least change in planned operations and systems.

Cadmium and gadolinium have compatibility problems with the lower limit on pH set at 7.5 and planned air-saturated water cleanup systems. These problems may be surmountable, but it is unlikely that they would be entirely solved in time to meet the recovery schedules. Their main advantage is that the cost of these elements is comparable to that of boron; however, these costs would be overwhelmed by the cost of the procedure for replacement of the current reactor coolant. In the case of cadmium, there would also be an increase in processing costs.

Samarium is eliminated from further consideration because of its large relative cost, as well as incompatibility problems similar to those of gadolinium and the difficulty obtaining the required amount. Europium is eliminated due to its tremendous cost. As for lithium, the combination of relatively high cost and the nitrate hazard make it an unsuitable alternate.

The use of insoluble absorbers, although ostensibly desirable from the viewpoint of the poison concentrations achievable, is not meaningful or practical in the core geometry as it is now known. There are serious radwaste handling problems in terms of the volume that would be generated. Insolubles also present problems in handling and in assuring adequate concentrations at specified locations. When insolubles were originally conceived as possible neutron absorbers to achieve the k_{eff} criterion, the core was envisioned as an array of damaged fuel assemblies hanging more or less in place. The insoluble absorbers were proposed to fill voids created during the removal of assemblies, thus preventing reconfiguration of the fuel as well as reducing reactivity. Recent video and sonar inspections show that the damage to the fuel assemblies is more extensive and the removal techniques have been modified accordingly. The use of insolubles to fill void spaces on a large scale is no longer necessary or advisable since it will reduce the effectiveness of the hydrocyclone vacuuming. General use of insoluble absorbers is not recommended for the purpose of achieving the k_{eff} criterion, although their use for specific applications may be justifiable.

2.4 Solubility of Boron in the Reactor Coolant

Solubility in the RCS and its auxiliary systems is dependent upon other solutes, temperature, and pH. Solubilities of pure sodium borate solutions were examined and compared with experimentally determined solubilities in RCS samples. The results show that the RCS and its auxiliary systems can, from a solubility standpoint, safely accommodate the boron concentrations deemed necessary from a criticality standpoint.

TABLE 4. COST AND AVAILABILITY OF INSOLUBLE ABSORBERS

Substance	Unit Material Cost ($/lb)	Estimated Amount Required (lbs)[a]	Total Estimated Cost ($)	Available within 6 months
32 wt.% Boron in polyethylene matrix (60% packing)	26	85,400	2,000,000	Yes
40 wt.% Boron in silicone binder (60% packing)	16	130,000	2,000,000	Yes
B_4C pellets (60% packing factor)	134	225,000	30,000,000	Yes
5 wt.% B_4C/Al_2O_3 Pellets (60% packing)	16	225,000	3,600,000	Yes
Borosilicate glass Raschig rings - 3 wt.% B (364 pieces/ft^3)	3.9	94,000	3,600,000	Yes

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a. Based on 2000 ft^3 and stated packing factor.

As discussed in section 2.1 and 2.5, the RCS is essentially a pure sodium borate solution and should have approximately the same equilibrium solution chemistry as the sodium borates.

Both standard industry literature and our own experiments show that the solubility of boron in buffered solutions is substantially higher than the concentration required to maintain the reactor in a subcritical condition. Figure 1 summarizes the solubility data for boron at 0°C and 10°C; the two solubility curves are intersected by six analytical curves (iso-pH lines) that relate B and Na concentrations at fixed pH in unsaturated solutions.[16] (See Section 2.5.) The following information is obtained from this figure:

- The solubility of boron increases with temperature.
- At a pH of 7.8 and 7.5 and a temperature of 50°F (the minimum temperature allowed by the Technical Specifications in the RCS), boron solubility is 11,000 ppm and 15,500 ppm respectively.

In addition, two solubility experiments were performed on actual reactor coolant samples. A sample was borated to a concentration greater than 9,700 ppm, pH adjusted to 7.8, and the temperature lowered to 36°F. No precipitation of boron occurred.[17] In a second experiment performed at the University of Maryland, the solubility of boron in a reactor coolant sample was determined at a pH of 6.5, 7.0 and 7.5. The solubility of boron was found to be 10,200 ppm, 17,300 ppm and 17,700 ppm, respectively.[18]

In summary, both literature data and recent experimental data support the view that boron solubility under all conditions of interest is in excess of any boron concentrations that may be required to maintain the reactor in a subcritical condition.

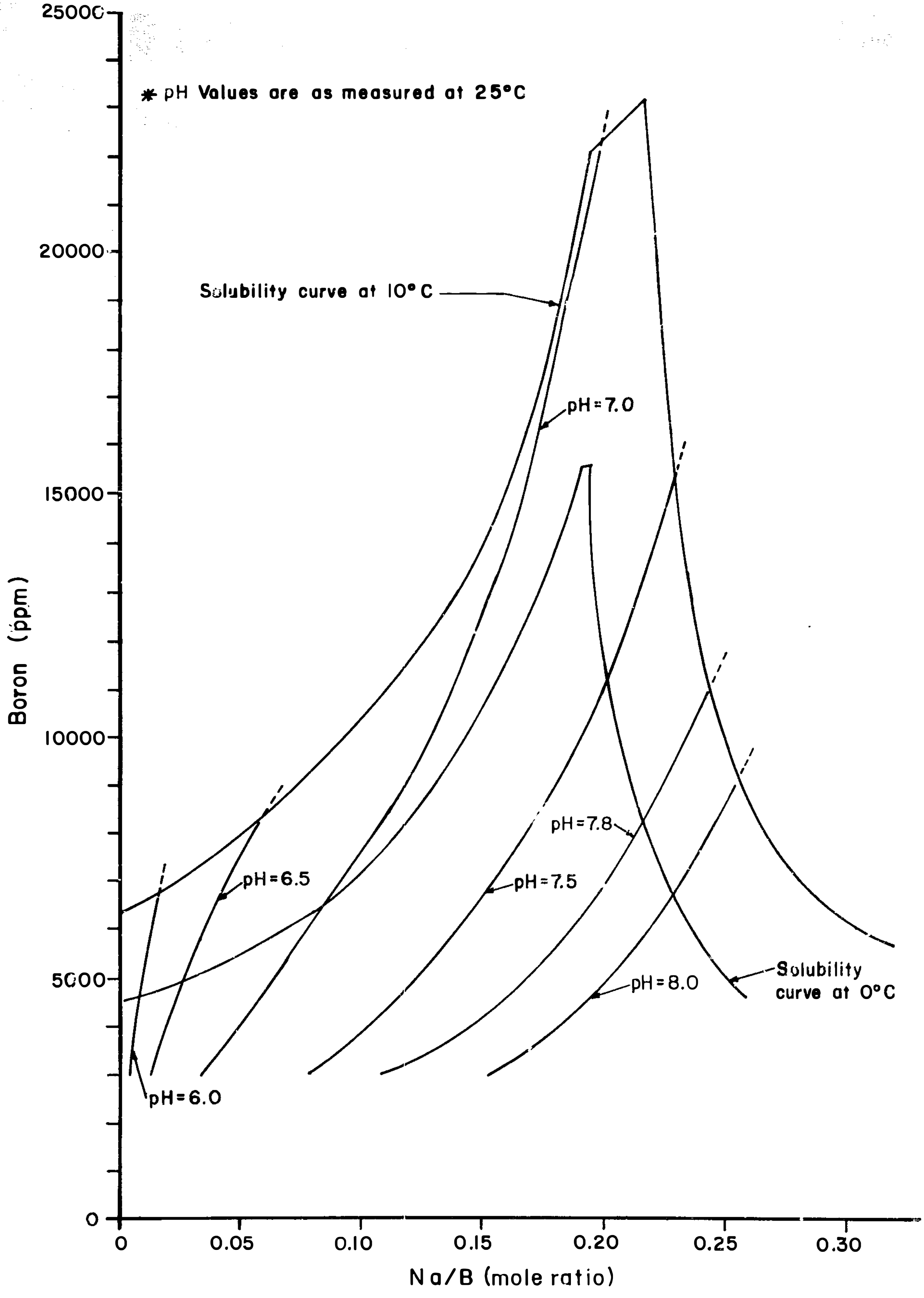

Figure 1. Solubilities of sodium borate solutions.

2.5 pH and Variations in Sodium and Boron Concentrations

Any decision to change the RCS water chemistry requires an understanding of how the pH and both the reactor coolant processing techniques and the cost will be affected. Boron concentration, sodium concentration, and pH are closely linked. pH, a major factor in corrosion protection, can be significantly changed by perturbations in the boron concentration. Maintaining the pH while increasing the boron concentration is accomplished by the addition of sodium hydroxide. The coolant processing cost is proportional to the sodium concentration. This section compares experimental data relating pH, boron, and sodium in the reactor coolant with similar analytical data for a pure boric acid/sodium hydroxide aqueous solution. Because sodium hydroxide and boric acid are the major contributors to the ionic strength of the coolant, the pH dependence on boron and sodium concentration should be similar in the two systems.

The combined effect of sodium hydroxide and boric acid on the pH of the reactor coolant was experimentally determined.[19] A 100 ml coolant sample was titrated with sodium hydroxide to several different concentrations of sodium. The boron remained constant at 3790 ppm and the pH was measured at each sodium concentration. Similar experiments were performed using pure water solutions of NaOH and H_3BO_3.[20] In Figure 2, these two sets of results are compared with analytical curves for the pure NaOH-H_3BO_3 solutions; these analytical curves are derived using the equilibrium constants of Mesmer, et al.[21] The experimental points are consistent with the analytical curves, indicating that the pH of the RCS is primarily dependent on the sodium hydroxide and boric acid concentrations.

According to Figure 2, the boron concentration in the RCS can be increased from the current level (≈ 3800 ppm) to 4500 ppm without adding sodium hydroxide, provided the pH is permitted to drop from its current level of 7.8 to 7.5; thus, increases in the boron concentration with appropriate drops in pH will not affect processing costs. Figure 2 also shows that lowering the pH from 7.8 to 7.5 reduces the required sodium concentration 30% at the current boron concentration of 3800 ppm. Further, by lowering the pH from 7.8 to 7.0, the sodium concentration is reduced by 67%. Processing costs could be reduced by similar percentages. (See Section 5.2 for a discussion of operating costs.) At pH = 6.0, the sodium requirements are 5% of those at pH = 7.8, but at this low sodium level, other factors dominate processing costs.

Lowering the pH below 7.5 is prohibited by the Technical Specifications; however, the significant savings in processing costs may lead to a re-evaluation of the pH specification especially if the change is accompanied by other benefits. A study of corrosion effects necessary to support a pH change in the Technical Specifications is beyond the scope of this report. Furthermore, increasing carbonate concentration, which will occur under aerated conditions, increases the sodium concentration required to maintain a specified on pH. It also reduces the sensitivity between the concentration of NaOH and pH.

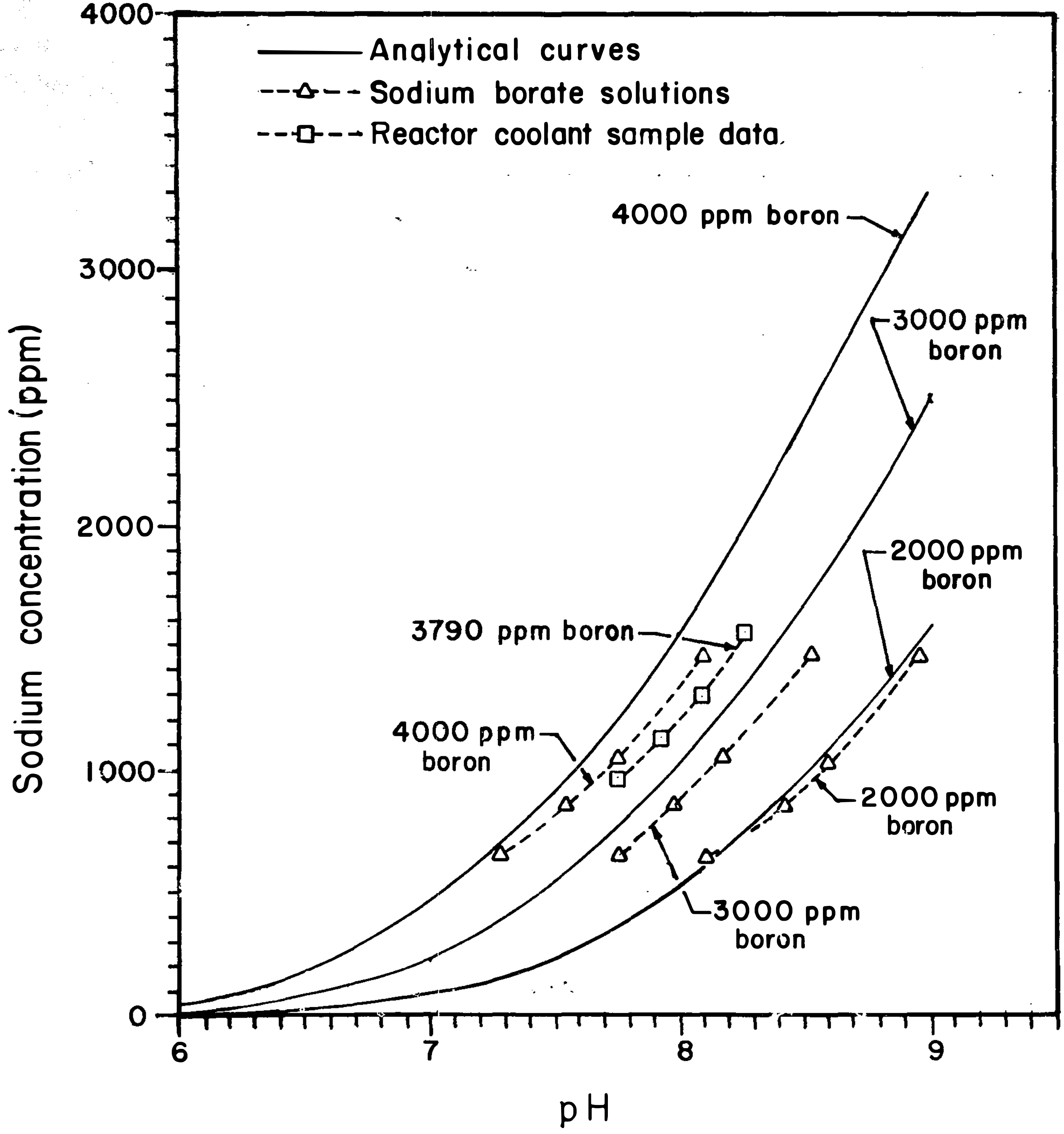

Figure 2. Sodium concentration as a function of pH in boric acid solutions for experimental data and theoretical curves.

The following are key elements in management decisions regarding proposed changes the RCS boron concentration:

- The pH of the reactor coolant is dependent upon the boric acid and sodium hydroxide concentrations and can be obtained from published information on pure boric acid/sodium hydroxide aqueous solutions.
- The RCS boron concentration can be raised to approximately 4500 ppm without addition of sodium hydroxide and without violating the Technical Specification limit of pH $\geq$ 7.5.
- A significant savings in processing costs is possible if the pH of the RCS is reduced from 7.8 to 7.5.
- The Technical Specification limit for pH should be re-evaluated with a view toward reduction in the sodium hydroxide requirements, provided savings in cost and man-rem are significant, and the incremental corrosion risks are trivial.

3.0 CRITICALITY ANALYSES

This chapter details the calculations performed at Oak Ridge National Laboratory to determine the amount of absorber required to reach a k_{eff} of 0.95. The neutron multiplication factors were calculated for the analytical model, which is based on assumptions discussed in Section 3.1. Discussion of the model is followed by a brief description of the analytical methods, specifically the computer codes, used for the calculations (Section 3.2). Section 3.3 gives a summary of the results provided by ORNL, showing that the k_{eff} criterion, devised for the purposes of this study only, is met at approximately 5500 ppm boron.

3.1 Model for Calculations

The model consists of the as-built TMI-2 reactor with the changes listed below. The changes were made with intent of increasing reactivity to a level beyond that of any core configuration that may arise during defueling, thereby leading to a conservative, i.e. high, estimate of the boron concentration required to ensure that the reactor remains subcritical during these operations. In addition, the model has a relatively simple geometry which can serve as the basis of reliable calculations.

- Three wt.% ^{235}U enrichment as UO_2 in all fuel pins.

  The original TMI-2 core consisted of three zones of different enrichments, the average of which is 2.57 wt.% ^{235}U.[22] The maximum enrichment in the original core was 2.97 wt.% ^{235}U.

- All pins intact.

  This assumption allows for reliable calculations of known geometries. It eliminates speculation as to the accuracy of the model with respect to current core configuration. Indeed, any resemblance between the current core configuration and those which might arise during defueling is irrelevant.

- Pitch optimized; i.e., pitch adjusted to obtain maximum reactivity for a given boron concentration.

  Adjustment of the pitch (the spacing between nearest fuel pins) changes the fuel-to-moderator ratio, which in turn affects reactivity. The optimum pitch is a function of boron concentration.

- Fuel and moderator at room temperature.

  As temperature decreases, reactivity increases. This pattern of temperature dependence has been found to be true for the moderator[23] as well as for the fuel. The effect on fuel is related to the temperature effect on the resonance absorption of ^{238}U. The assumption could have been made more conservative by decreasing the temperature to the lower Technical Specification limit of 50°F; however, as shown in Section 3.3, the difference between the neutron multiplication factors at room temperature and 50°F is small.

- No credit for burn-up.

  Burn-up is a measure of the percentage of fissile nuclei (specifically ^{235}U) consumed during fission. Burn-up causes a decrease in reactivity because of the conversion of neutron-producing fuel into neutron absorbing fission products. The damaged core underwent 94 equivalent full-power days before the accident.

- Control rods and structural materials neglected.

  The designed effect of control rods is to absorb neutrons, thus decreasing reactivity. Structural materials also decrease reactivity since their neutron moderation properties have less of an impact than their neutron absorption properties.

- The boron concentration in the primary coolant was varied from 1500 to 7500 ppm.

  This allows the construction of a curve of boron concentration versus neutron multiplication factor over the range of interest.

- A case with and a case without zircaloy cladding for each boron concentration.

  Although inclusion of cladding generally tends to decrease reactivity,[23] this effect is not as obvious at high boron concentrations where zircaloy displaces boron (and moderator) which could have a larger neutron absorption effect than zircaloy; thus, the presence of zircaloy could cause less of a net decrease in reactivity than the presence of boron.

It should be noted that, although these assumptions were deemed sufficiently conservative to meet the objectives of the study, it is possible to devise conditions which would make the model more reactive.

3.2 Analytical Methods

The computer programs used to calculate the neutron multiplication factor of the model are parts of the modular code system for performing Standardized Computer Analyses for Licensing Evaluation (SCALE). This system is composed of several automated analytical sequences or control modules which perform criticality, shielding, and/or heat transfer calculations with a minimum of required input from the user.[24]

The control module, Criticality Safety Analysis Sequence No. 1 (CSAS1), was used in the analysis of k_{eff} for the one-dimensional, i.e. infinite, systems. This module comprises two cross section processing codes, NITAWL-S and BONAMI-S, and a one-dimensional, discrete-ordinates, transport code (XSDRNPM).[25] NITAWL-S uses the Nordheim Integral Treatment for performing problem-dependent resonance shielding,[26] while BONAMI-S uses Bondarenko calculations for resonance self-shielding.[27] Both of these codes were used to process the 27 group cross section sets that were selected from the master cross section library. The control module (CSAS1) itself performs the calculation of the number densities for each nuclide, and determines the Dancoff factors for the resonance self-shielding calculations.[25]

For the multidimensional (finite) systems, the Criticality Safety Analysis Sequence No. 2 (CSAS2) was used. This control module processes the 27 group cross section sets using BONAMI-S and NITAWL-S as well as calculating the number densities and Dancoff factors.[28] These data are then used in KENO V, a Monte Carlo criticality program for determining k_{eff} of finite systems.

3.3 Results of Criticality Analyses

The results of the calculations for the 3 wt. % enriched uranium dioxide fuel pins are presented on Tables 7 and 8. Table 7 reports the data for the cases with the zircaloy cladding; Table 8 reports the data for the cases without zircaloy cladding (Reference 7). Both sets of results are for pins in their optimum borated water spacing. Since the only materials present in these analyses were UO_2, zircaloy (for the cases with cladding), B and H_2O, those 17 locations in each assembly that had instruments or poison rods in the undamaged core were assumed to contain borated water in the calculational model.[29]

Figure 3, is a graphical representation of the data in Tables 7 and 8, showing that the neutron multiplication factors produced from the cases without the cladding are higher than those from the cases with the cladding. The boron concentration for the k_{eff} criterion is approximately 5,500 ppm. The boron concentrations 4,500 ppm and 4,200 ppm correspond to a k_{eff} of 0.98 and 0.99, respectively. In reporting these data, the authors urge the reader to recall the conservatism of the model, based on the assumptions listed in Section 3.1.

ORNL examined the temperature effect on the finite system of unclad fuel pins at a lattice pitch of approximately 1.53 cm and a boron concentration of 1700 ppm. These results are reported on Table 9 and were taken from Reference 7. The difference in k_{eff} between 68°F and 50°F is 0.00012, which is well within the uncertainty of the Monte Carlo technique. Since the temperature

TABLE 7. U(3)O_2 PIN ANALYSIS WITH OPTIMUM BORATED WATER SPACING WITH CLADDING[a]

Boron (ppm)	Lattice Pitch (cm)	$k_{eff} \pm \sigma$ (finite geometry)
3443	1.2031	1.00306 ± .00245
4500	1.1850	0.95589 ± .00277
5000	1.1700	0.93572 ± .00303
6500	1.1450	0.89220 ± .00261
7500	1.1250	0.86728 ± .00269

---

[a] Results are taken from Reference 7.

TABLE 8. $U(3)O_2$ PIN ANALYSIS WITH OPTIMUM BORATED WATER SPACING WITHOUT CLADDING[a]

Boron (ppm)	Lattice Pitch (cm)	$k_{eff} \pm \sigma$ (finite geometry)
3443	1.0922	1.02480 ± .00271
4500	1.0500	0.97993 ± .00313
5000	1.0400	0.96443 ± .00279
6500	1.0160	0.92813 ± .00267
7500	1.0160	0.89979 ± .00301

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a. Results are taken from Reference 7.

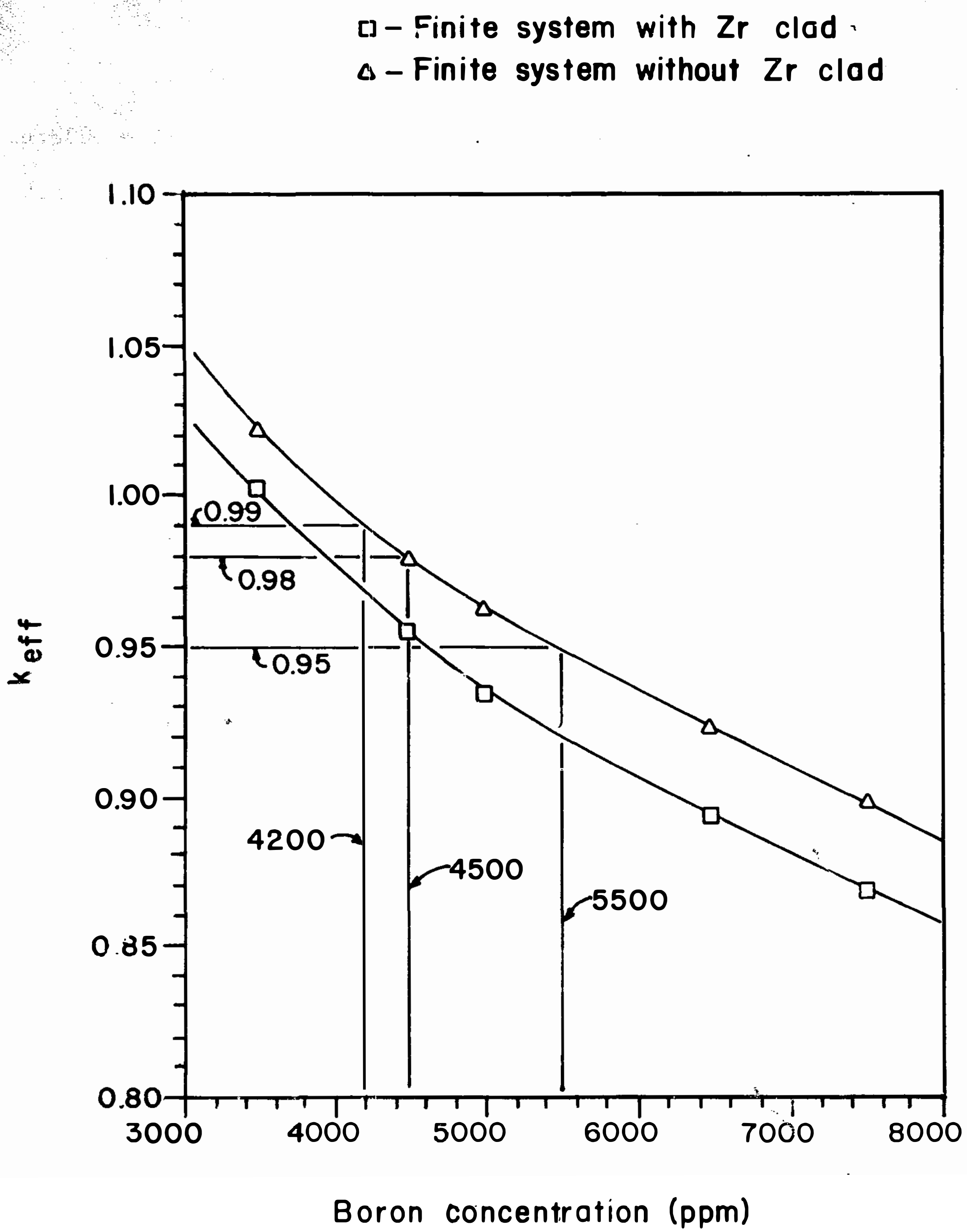

Figure 3. Calculated neutron multiplication factors for the finite reactor as a function of boron concentration.

TABLE 9. THE CALCULATED k_{eff} FOR A FINITE SYSTEM OF UNCLAD FUEL PINS AT A LATTICE PITCH OF 1.53 cm AS A FUNCTION OF TEMPERATURE[a]

Temperature (°F)	$k_{eff} \pm \sigma$
68	0.99979 ± 0.00256
50	0.99991 ± 0.00269
32	1.00722 ± 0.00270

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[a] Results taken from Reference 7. Boron concentration for all three cases was 1700 ppm.

effect for the system of lattice pitch 1.53 cm is similar to that of the optimum borated-water lattice spacing, the assumption of room temperature for the model does not significantly detract from its conservatism.

ORNL was also asked to calculate the neutron multiplication factor for a zero-power startup configuration of the original TMI-2 core to demonstrate the applicability of the analytical method. In Reference 7, they report the conditions at critical as:

- Coolant: 532°F, 2200 psi, $\rho = 0.77$
- Fuel: 532°F
- Control rods out
- Axial power shaping rods centered
- 1500 ppm boron
- Calculated $k_{eff} = 0.9973 \pm 0.0028$.

These conditions are in good agreement with the initial critical conditions of the original TMI-2 core.[30]

4.0 ENGINEERING FOR BORON ADDITION

The choice of higher boron concentration for the RCS must be accompanied by an evaluation of the preparation and subsequent addition of a more concentrated solution to the reactor coolant system. This evaluation is presented in 4.1. The reactor facility is equipped with a boric acid mix tank and a pump whose purpose is to add concentrated boric acid solutions to either the borated water storage tank or directly to the reactor coolant system via the makeup and purification system. However, with the reactor in its present condition, access to some locations and operation of some systems are restricted because of safety concerns. Consequently, planning is required to increase the soluble poison concentration in the reactor coolant system without unacceptable delay in the recovery program. The methods, and concomitant limitations and advantages are discussed in Section 4.2.

4.1 Method of Mixing Solutions

The boric acid mix tank (BAMT) is the easiest and most convenient place to mix solutions and transfer them in batches to various systems within the reactor complex. The BAMT has a capacity of 7500 gal and is provided with a mechanical mixer and a 50 kW heater. All lines leading into and from the BAMT are heat traced to prevent possible crystallization of the boric acid solution at temperatures below 90°F. The maximum boron concentration recommended in the BAMT is 12,200 ppm. The boric acid pumps (BAP) are hydrotube-pulsafeeder pumps capable of pumping 10 gpm at 231 ft of developed head. The BAMT and BAP can be used to mix an appropriate number of batches of highly concentrated boric acid solutions which can then be transferred to either the borated water storage tank or to the RCS. The concentration of boric acid in each batch is checked by sample analysis.

4.2 Method of Addition to RCS

In order to increase the boron concentration in the RCS, the following criteria and limitations must be understood and maintained.

- All water in the reactor coolant system must be at or above the poison concentrations needed to keep the core subcritical under all defueling conditions.
- In the partially drained condition of the RCS, the maximum bleed/feed flow rate is 2-3 gpm.
- In the partially drained condition, a bleed/feed cycle on the RCS will not flush the water in the primary side of the once-through steam generators, the pressurizer or in certain portions of the hot and cold leg pipes.
- The ^{137}Cs activity in the present reactor coolant will prevent it from being stored in any tank other than the waste holdup tanks.
- The bleed/feed flow rate with the RCS at 60 psig is 14 gpm.

The RCS in the partially drained condition contains 55,000 gal of water at 3750 ppm boron. The total volume of the RCS with the reactor vessel head installed is 90,000 gal; therefore, if the present void volume of the RCS were filled with water at a boron concentration of 12,000 ppm, a mean concentration of 7,000 ppm would result. This can be accomplished by making [illegible] five batches of solution in the boric acid mix tank of 12,000 ppm boron each and pumping it via the makeup line to the RCS. The RCS must then be allowed to circulate to obtain complete mixing.

A second method of increasing the boron concentration in the RCS is to perform a bleed/feed cycle with the RCS filled. Eventually all the water which could come in contact with the core will have to be increased in boron to the concentration specified to prevent core criticality. The present TMI-2 defueling plans require that the refueling canal and the spent fuel canal be flooded to an elevation of 347 ft, 6 in. This large volume of water plus that associated with various tanks needed to process it is 914,000 gal. This volume of water would be established and stored in the BWST; therefore, filling the BWST with water at the proper concentration buffered with sodium hydroxide to a pH > 7.5 is a convenient and effective means of eventual boration of all the water to be used in the defueling program. With the BWST at the proper concentration, water can be pumped from the BWST to one of the waste holdup tanks. Approximately 75,000 gal of water can be stored in these tanks. By means of a normal bleed/feed process, the water in the RCS can be replaced with the water stored in the RCBT. The water from the RCS can then be processed through the SDS to remove radionuclides.

If it is necessary to increase the RCS boron concentration in the near future, a variation in the second method can be utilized: namely, increasing the boron concentration in the waste holdup tank only. This variation does not require the additional time and expense of preparing the entire BWST to accommodate the new boron concentration. The BWST could be brought up to the increased boron concentration at a later date.

5.0 ECONOMICS

The economics of absorber selection depends on both material and operating costs. Material costs consist of the purchase price of absorber plus the cost of transportation to the site (5.1). Operating costs are those associated with preparation of a uniform solution of the absorber in the reactor coolant plus additional costs, if any, of decontaminating the reactor coolant during the TMI-2 defueling process. Consideration was also given to offsetting the costs by absorber selection or modifications in the operating methods. These discussions are found in section 5.2.

5.1 Material Costs

The present TMI-2 defueling plan requires that a total water volume of 914,000 gal be stored with RCS equivalent composition. The compatibility of additional boron or fully enriched boron is known by virtue of its current use in the RCS, as well as the fact that boron solubility far exceeds the concentrations under consideration. Isotopic distribution has no practical effect on its chemistry, but increasing the boron concentration increases the sodium hydroxide required to control the pH, thus increasing the processing costs. Since less fully enriched boron is required to achieve the same neutron absorption as boron (642 ppm ^{10}B[a] per 3500 ppm boron), the effect on processing costs would be less than with boron. Therefore, consideration was given to purchasing 80% ^{10}B[b] material as well as boron (20% ^{10}B). Table 10 illustrates this comparison.

It is evident that the material costs of highly enriched boron are extremely high compared to those of ordinary boric acid crystals. If an overall savings is to be made using enriched boron, the material cost would have to be offset by decreased operating costs associated with the decreased sodium hydroxide required to maintain pH, thereby permitting the processing of a greater volume of water per zeolite bed.

5.2 Operating Costs

Present defueling plans schedule purification of reactor coolant from August 1984 through December 1987 (41 months) and purification of canal water from January 1986 through December 1987 (20 months). The boron concentration will be maintained until the end of defueling, December 1987. The rate of processing is dependent upon the rate that soluble ^{137}Cs appears in the water. This rate is currently observed to be 0.01 mCi/ml-day. In order to maintain the ^{137}Cs concentration in the RCS water < 0.1 mCi/ml, a flow rate of 50,000 gal per week through the SDS is required. Consequently, in 41 months, 8.8×10^6 gal of water would be processed. Similarly, the purification of the canal water requires the processing of 16×10^6 gal of water in 24 months to maintain the ^{137}Cs concentration <0.02 mCi/ml.

A comparison of boron and enriched boron material costs (both in the form of boric acid) and the penalty for increasing the sodium hydroxide concentration reveal that the operating cost penalty never approaches the material cost (See Table 11); therefore, the least expensive means of increasing the neutron absorber in the reactor coolant is boric acid (20% ^{10}B).

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a. Fully enriched boron.
b. This enrichment was determined to be the most cost effective.

TABLE 10. MATERIAL COST SUMMARY

Substance	Increased Boron Concentration[a] (ppm)	Amount Req'd (kg)	Boron Unit Cost ($/kg)	Absorber Cost ($)	NaOH Req'd (kg)	NaOH Unit Cost ($/kg)	NaOH Cost ($)	Total Material Cost ($)
B(20% ^{10}B)	3250	6.5x10^4	2.15	140,000	12,000	2.31	27,700	168,000
	2000	4x10^4	2.15	86,000	7,500	2.31	17,350	103,000
	1000	2x10^4	2.15	43,000	3,480	2.31	8,000	51,000
B(80% ^{10}B)	590	1.6x10^4	684	11x10^6	1,012	----[b]	----[b]	1.1x10^7
	367	1.0x10^4	684	6.8x10^6	630	----[b]	----[b]	6.8x10^6
	183	0.5x10^4	684	3.4x10^6	315	----[b]	----[b]	3.4x10^6

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a. Quantities and costs are based on adding additional absorber material to 914,000 gal which is at 3750 ppm boron and 1000 ppm NaOH at a pH of 7.8.

b. Negligible.

TABLE 11. OPERATING COST SUMMARY

	Total Fluid Processed (gal)	Cost Per Gallon ($)	Expected Operating Costs ($)	Operating Cost Increase 1000 ppm B ($)	 2000 ppm B ($)	 3250 ppm B ($)
RCS	8.815×10^{6}[a]	0.21[a]	1.85×10^{6}	1.1×10^{6}	2.3×10^{6}	3.7×10^{6}
Fuel Canal	16×10^{6}	0.032[b]	5.12×10^{5}	2.9×10^{5}	6.4×10^{5}	1.03×10^{6}
			Total	1.4×10^{6}	2.9×10^{6}	4.7×10^{6}

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a. SDS cleanup system
b. DWCS cleanup system

As shown in Section 2.5, the operating costs can be further reduced by lowering the pH. If the pH were lowered to 7.5 approximately 300 ppm of NaOH could be removed from the RCS fluid which would decrease operating cost 30%. While further reductions in pH are also possible with the current demineralizers, they involve the costly removal of sodium which would have to be charged against other benefits that would be cited in favor of such an action.

6.0 CONCLUSIONS

A summary of the principal findings of the study is presented in Section 6.1. The bases for the principal findings are summarized in Section 6.2.

6.1 Summary of the Principal Findings

- Other than boric acid, the soluble neutron absorbers examined in this work have cost and physicochemical compatibility problems which preclude their use in the TMI-2 reactor coolant system.
- Insoluble neutron absorbers are an impractical means of providing a well-controlled distribution of added poison during defueling operations because of the core geometry and the nature of the core damage.
- Boron in the form of boric acid is the absorber recommended for use in the RCS in view of its proven effectiveness and minimal impact on water cleanup systems.
- The effect of pH on sodium requirements and processing costs is strong.
- The k_{eff} criterion (devised for the purposes of this study only) is met at 5500 ppm boron.
- Boron concentration can be increased using existing equipment and established techniques; however, the increase must take place prior to head-lift to ensure complete mixing.

6.2 Summary of Bases for the Conclusions

The investigation of the physicochemical properties of soluble alternate poisons reveals that despite some potential benefits each has overriding incompatibilities or uncertainties precluding its use in this reactor coolant system. The soluble forms of alternate poisons investigated were nitrates or sulfates. The use of any nitrate would require modification of the water cleanup systems to prevent the possibility of rapid uncontrolled oxidation in the organic demineralizers. Concern about the use of sulfates exists due to their potential reduction to species which could cause long-term corrosion effects. The risks associated with both concerns are probably minor, but there is insufficient time to lay these valid concerns to rest.

The soluble forms of gadolinium, europium, and samarium precipitate at pH $>$ 6.0, causing a local poison concentration depression, a condition unacceptable from a criticality safety standpoint. This fact renders impossible the replacement of the current reactor coolant (pH $>$ 7.5) by a bleed/feed method, which is currently the only method of coolant replacement. Cadmium has a slight tendency to deposit on primary system structural components; it precipitates at pH $\geq$ 7.7 in the absence of air and at even lower pH under aerated conditions. A preliminary investigation into lowering the Technical Specification limit on pH reveals that the requisite examination of corrosion effects is beyond the scope of this report. Furthermore, it is unlikely that this examination could be accomplished in time to receive approval of the Technical Specification change, lower the pH, and introduce a new solution without causing a delay to the defueling schedule.

Lithium salts in high concentrations present problems of precipitation of insoluble borates during bleed/feed operations, as well as the fire hazards common to all nitrates.

The use of an alternate poison requires the development and testing of monitoring capabilities, possibly causing delays in the defueling schedule. None of the alternate poisons investigated have advantages which would justify delaying the defueling to solve these problems.

The use of insoluble absorbers is not meaningful or practical in the damaged core as it now exists and in the configurations it can assume during fuel removal operations. There are severe handling problems with respect to their addition at required positions and assurance of adequate concentrations everywhere at all times. They also create a large volume of radwaste.

Because there is no economic incentive to justify the change to an alternate poison and boric acid does not have the chemical compatibility problems of the other soluble neutron absorbers, there is no practical alternative to boric acid. The solubility limit is well above the concentration required to achieve adequate shutdown margin. Its impact on the water cleanup system is well understood and its use does not require the alteration or re-engineering of the system. There is some decrease in the capacity of the demineralizers to absorb cesium because of the additional sodium that must be added to maintain the pH along with the additional boric acid.

Investigations show that a small decrease in the pH leads to a large decrease in sodium requirements. Since processing costs are almost directly proportional to sodium concentrations, the pH should be maintained as close to the lower Technical Specification limit as possible. Two facts relating to sodium requirements should be noted: (a) sodium requirements are nonlinear with boron concentration and (b) saturation of the primary coolant with carbon dioxide from exposure to air will cause the formation of carbonates, resulting in some increase in the sodium concentration required to maintain the pH.

ORNL calculations performed on the selected model of the core indicate that the k_{eff} criterion ($k_{eff} = 0.95$), devised for the purpose of this study only, is met at 5500 ppm boron. In view of the highly conservate assumptions associated with the model, management would be justified in establishing a higher k_{eff} and a lower boron concentration as conditions which assure subcriticality under all defueling conditions. Other neutron multiplication factors and corresponding boron concentrations of interest based on the study model are: $k_{eff} = 0.98$ at 4500 ppm boron and $k_{eff} = 0.99$ at 4200 ppm boron.

Increases in the RCS boron concentration can be made by bleed/feed methods using existing equipment and established techniques; however, the increase must be made prior to head lift. The reason is that the entire primary coolant system be at the same boron concentration. The only way to achieve uniformity in the boron concentration rapidly is to refill and repressurize the system, thus assuring mixing of the entire system fluid through a combination of natural circulation and the pumping action associated with the bleed/feed process.

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