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**SOME ASPECTS OF PRIMARY AND SECONDARY WATER  
CHEMISTRY IN CANDU REACTORS**

**Quelques aspects de la chimie de l'eau primaire et secondaire  
dans les réacteurs CANDU**

**J.E. LeSURF**

Presented at Symposium on Water Chemistry In and Out of Reactors American Chemical Society National Meeting,  
Miami, Florida, 1978 Sept. 11-16

Chalk River Nuclear Laboratories

Laboratoires nucléaires de Chalk River

Chalk River, Ontario

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Chalk River, Ontario K0J 1J0  
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Quelques aspects de la chimie de l'eau primaire et  
secondaire dans les réacteurs CANDU\*

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Résumé

On passe brièvement en revue la chimie de l'eau dans les divers circuits des réacteurs CANDU. Puis, on souligne cinq aspects particuliers de travaux récents:

- (i) Croissance du champ de rayonnement: des études faites en réacteur et hors réacteur ont permis de mettre en corrélation la chimie de l'eau, le dépôt de produits de corrosion sur les gaines de combustible et la contamination subséquente des surfaces hors cœur.
- (ii) Solubilité des oxydes métalliques: on a recours à de nouvelles techniques pour mesurer les solubilités des oxydes métalliques dans les conditions des circuits primaires.
- (iii) Décontamination: l'emploi de l'eau lourde comme caloporteur dans les réacteurs CANDU a conduit au développement d'une stratégie unique en son genre de décontamination et d'une technique appelée CAN-DECON, qui a attiré l'attention des opérateurs de réacteurs à eau légère.
- (iv) Corrosion des générateurs de vapeur: des modèles mathématiques représentant la chimie de l'eau dans les parties massives et crevassées des générateurs de vapeur des centrales nucléaires ainsi que des expériences chimiques ont montré pourquoi la pénétration de l'eau de mer provenant des fuites du condenseur peut être endommageante et ont permis de mettre au point une méthode rapide pour évaluer d'autres chimies d'eau de chaudière.
- (v) Contrôle automatique de la chimie de l'eau d'alimentation: l'analyse chimique automatique in-situ et le contrôle par ordinateur de la chimie de l'eau d'alimentation donnent un traitement entièrement volatil pour un fonctionnement normal avec de l'eau d'alimentation pure et une addition soigneusement contrôlée de phosphate de sodium lorsqu'il y a une pénétration décelable d'eau de mer provenant des fuites du condenseur.

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\*Rapport présenté au Symposium sur la chimie de l'eau en réacteur et hors réacteur du Congrès national de l'American Chemical Society tenu à Miami, Floride, du 11 au 16 septembre 1978.

SOME ASPECTS OF PRIMARY AND SECONDARY WATER CHEMISTRY  
IN CANDU REACTORS\*

J.E. LeSurf

Abstract

A brief review of the water chemistry in various circuits of CANDU reactors is given. Then, five particular aspects of recent work are highlighted:

- (i) Radiation Field Growth: in-reactor and out-reactor studies have related water chemistry to corrosion product deposition on fuel sheaths and subsequent contamination of out-core surfaces.
- (ii) Metal Oxide Solubility: novel techniques are being used to measure the solubilities of metal oxides at primary circuit conditions.
- (iii) Decontamination: the use of heavy water as coolant in CANDU reactors led to the development of a unique decontamination strategy and technique, called CAN-DECON, which has attracted the attention of operators of light-water reactors.
- (iv) Steam Generator Corrosion: mathematical modelling of the water chemistry in the bulk and crevice regions of nuclear steam generators, supported by chemical experiments, has shown why sea water ingress from leaking condensers can be damaging, and has provided a rapid way to evaluate alternative boiler water chemistries.
- (v) Automatic Control of Feedwater Chemistry: on-line automatic chemical analysis and computer control of feedwater chemistry provides All Volatile Treatment for normal operation with pure feedwater, and carefully controlled sodium phosphate addition when there is detectable sea-water ingress from leaking condensers.

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\* Paper presented at Symposium on Water Chemistry In and Out of Reactors, American Chemical Society National Meeting, Miami, Florida, 1978 Sept. 11-16.

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SOME ASPECTS OF PRIMARY AND SECONDARY WATER CHEMISTRY  
IN CANDU REACTORS

J.E. LeSurf

1. AN INTRODUCTION TO THE WATER CHEMISTRY OF CANDU REACTORS

Water performs three basic functions in any water-cooled nuclear power reactor:

- (i) it moderates "fast" neutrons to a "thermal" energy where they can be captured by the uranium nucleus and thus propagate the fission chain reaction,
- (ii) it takes heat away from the fuel and produces steam,
- (iii) the steam is used to drive a turbine-generator to produce electricity.

In a Boiling Water Reactor (BWR), only one water circuit is used to perform all three functions. In a Pressurized Water Reactor (PWR) the primary coolant acts as moderator and heat transport fluid, but steam is produced in a secondary circuit. A CANDU-PHW\* reactor has a separate water circuit to perform each of the three functions. The moderator and primary coolant are heavy water ( $D_2O$ ), while the secondary circuit is filled with ordinary water ( $H_2O$ ). The separation of moderator and primary coolant is made possible by the use of pressure tubes in CANDU reactors, instead of a pressure vessel, as is used in the BWR and PWR designs. The separation of coolant and moderator simplifies the chemical control of each.

Figure 1 is a diagram of a CANDU reactor, drawn to emphasize the three principal water circuits.

The water chemistry of CANDU-PHW reactors has been discussed in detail elsewhere [1]. Only a superficial account will be given here as background to the techniques which form the body of this paper.

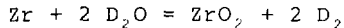
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\* CANada Deuterium Uranium Pressurized Heavy Water

## Primary Coolant Chemistry

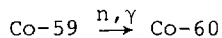
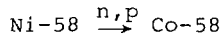
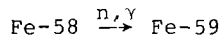
The chemistry of the heavy water primary coolant of a CANDU-PHW reactor is adjusted to minimize corrosion of materials in the circuit, both in-core and out-of-core.

The in-core components (fuel sheaths and pressure tubes) are made of zirconium alloys. Chemical reaction with heavy water produces zirconium dioxide and heavy hydrogen (deuterium).



The most serious consequence of such corrosion is accumulation of deuterium in the zirconium alloy component, which leads to embrittlement of the material if too much deuterium is absorbed.

The out-of-core pipes, pumps, valves and other components are made mainly of carbon steel. The steam generator tubes are made of a high nickel alloy. The most serious consequence of corrosion of these materials comes from the release of corrosion products (metal oxides) to the water. The oxides are carried into the core where they reside for about 10 days on average, becoming radioactive from neutron bombardment, e.g.



(Cobalt is present as an impurity in carbon steel and in nickel alloys. Also, some small areas of cobalt alloys are used on valve facings.)

The radioactive corrosion products redeposit on out-of-core surfaces. The radiation fields so produced hamper the routine operation, maintenance and repair of out-of-core components. Some ways of understanding and countering this problem are discussed in Sections 2, 3 and 4 of this report.

Corrosion of both in-core and out-of-core materials is inhibited by raising the pH of the coolant to about 10.5 by adding LiOD, and suppressing the radiolytic formation of oxygen by maintaining about 5 cm<sup>3</sup> D<sub>2</sub>/kg D<sub>2</sub>O dissolved in the coolant. No other chemicals are added to the primary coolant. A purification circuit consisting of heat exchangers, filters and ion

exchange resins minimizes the concentration of adventitious chemical impurities in the water.

### Moderator Chemistry

Light atoms are good moderators of fast neutrons. Hydrogen is the best, because its nucleus has virtually the same mass as that of the impinging neutron. Deuterium is next best (mass 2). Because the thermal neutron capture cross section of deuterium ( $\sim 0.5$  barns $^*/\text{cm}^2$ ) is so much less than that of hydrogen (322 barns/cm $^2$ ), heavy water (D $_2$ O) is used as the moderator for the CANDU-PHW reactors.

As with light water reactors, boric acid is used to control reactivity, but with the CANDU design the boric acid is added only to the moderator, not to the primary coolant. The pH of the moderator is lower than that of the primary coolant, and radiolytic oxygen (or oxidizing species) is usually present. Therefore carbon steel is not used, because it would corrode too rapidly.

The maximum permitted moderator temperature is 30°C, permitting a low pressure circuit design. The moderator tank (calandria) is a cylindrical vessel made of grade 304L stainless steel (19% Cr-8% Ni- $\sim 0.03\%$  C), with calandria tubes of zirconium alloys. The pipes and fittings (valves, pumps, tees, etc.) are all made of 18/8 stainless steel, using the low carbon (L-grade) variety when welding is required. The moderator cooler has moderator water through the tubes and site service water outside them. The tubes are made of nickel alloys.

Water chemistry is controlled by filters and a series of ion exchange resins, which remove impurities from the water (to inhibit corrosion and radiolysis) and add or remove boric acid as required for reactivity control.

### Boiler Water Chemistry

The secondary side of a nuclear steam generator (boiler) acts as a receptacle for all the non-volatile contaminants which enter the feed water or are produced in the boiler itself. In other words, it is a giant garbage can. Non-volatile contaminants may derive from:

- leakage of condenser cooling water into the steam condensate,

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\* 1 barn =  $10^{-28}$  m $^2$

- corrosion products from the condenser, feedwater heaters and connecting piping,
- corrosion products from the boiler itself.

Chemicals are added to the boiler feedwater or to the boiler water to protect surfaces against corrosion, to modify the nature of precipitates, and to counter the corrosiveness of chemical impurities which become concentrated in the boiler. Addition of hydrazine (to react with oxygen) and volatile amines (to elevate pH) results in an All Volatile Treatment (AVT) which is adequate and attractive when the boiler water is benign. When the boiler water becomes very corrosive (such as when sea-water leaks into the boiler feedwater through the condenser) more positive anticorrosive treatments are required.

Sections 5 and 6 of this report deal with understanding and controlling boiler water chemistry.

## 2. UNDERSTANDING THE GROWTH OF RADIATION FIELDS

Many studies have been made of the rate of growth of radiation fields caused by the spread of activated corrosion products around nuclear power reactors. In most of these studies the rate of field growth at existing reactors is measured, empirical equations are fitted to the data, and extrapolations to longer times or to other reactors are attempted by adjusting certain parameters in the empirical equations. Some of these studies have been reviewed by Lister [2].

At the research laboratories of Atomic Energy of Canada Limited (AECL)\* a more fundamental approach is taken. For each step, the mechanisms controlling corrosion, transport, deposition (in-core), removal and redeposition (out-core) are postulated and the postulates tested by specific experiments. If the postulated mechanisms are substantiated by the experiments, they are added to an overall activity transport model. The parameters used are mostly those relating to fundamental properties of metals and their oxides. This study has been extensively documented, both by summary reports and by detailed accounts of specific topics. A selection of papers which cover many (but not all) aspects is listed as references 3 to 18 inclusive.

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\* CRNL - Chalk River Nuclear Laboratories, Chalk River, Ontario  
WNRE - Whiteshell Nuclear Research Establishment, Pinawa,  
Manitoba



Activity transport is thought to proceed by the following steps:

- out-reactor surfaces corrode,
- corrosion products enter the coolant as particles and as ions in solution,
- the coolant transports the corrosion products to the core,
- corrosion products are deposited on in-core surfaces (primarily as particles), where they become radioactive,
- activated corrosion products redissolve in the coolant and are transported out-core,
- activated ions in the coolant exchange with ions produced from the corroding surface (or crystallize out on cooled surfaces), rendering the surfaces radioactive.

Each of these steps has been modelled and experimentally studied, so that we now have a sophisticated mathematical description of what happens under given circumstances. Good agreement has been found between earlier predictions of radiation fields and recent measurements at the Pickering and Bruce Nuclear Generating Stations, as illustrated in Figure 2.

An activity transport manual has been prepared which allows designers and operators of CANDU-PHW reactors to predict with confidence the effect on radiation field growth of certain actions, such as:

- changing the composition of materials of construction,
- changing coolant pH, temperature or flow rate,
- changing the on-power refuelling program.

### 3. METAL OXIDE SOLUBILITY

The previous section described how mathematical models are developed and tested. If those models are to be used to predict the growth of radiation fields, metal oxide solubilities must be known. Both theoretical and experimental advances into determining metal oxide solubilities have been made by AECL. The emphasis has been on determining the solubility of magnetite

in water between 200°C and 300°C, but the techniques used are applicable to other oxides, such as nickel ferrite, of which some study has been made.

### Theoretical Studies

A careful theoretical assessment of the solubility of metal oxides has been proceeding for more than 8 years. Publications have appeared regularly since 1972 [19 to 27]. The early work by Macdonald and co-workers was based on selecting the most reliable thermodynamic data available and interpolating missing values to calculate the solubility of metal oxides versus temperature and pH. In a recent paper [28] Tremaine and others have critically reviewed published data on Gibbs free energy and entropy for ferrous ions ( $\text{Fe}^{2+}$ ,  $\text{FeOH}^+$ ,  $\text{HFeO}_2^-$  and  $\text{FeO}_2^{2-}$ ). The most reliable values were used with the Criss-Cobble [29] principle to calculate the Gibbs free energies at 300°C and, hence, the solubility of  $\text{Fe}_3\text{O}_4$  in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  at 300°C as a function of the pH or pD measured at 25°C. Theoretical curves are given for the solubilities of magnetite versus pH for 100°C, 150°C, 200°C, 250°C, 285°C, 300°C, 325°C. In each case, appropriate experimental values from published literature are given. (Examples are given in Figures 3 and 4.)

The solubility/pH curves for magnetite at high temperatures pass through minimum values in the pH range 9 to 11. Experimental results are difficult to obtain and are subject to considerable error within this range. Many more, and more reliable, results exist for pH's below and above this range, where the solubilities are higher and correspondingly easier to measure. By showing that his theoretical numbers agree well with measured ones at low and high pH, Tremaine is able to enhance the confidence in his predicted values in the pH range 9 to 11 where experimental data are few and suspect.

The data of Sweeton and Baes [30] are commonly used when estimating activity transport phenomena. The AECL work discussed here concludes that the pH for minimum solubility of magnetite predicted by Sweeton and Baes is low (9.8 compared with 10.3 at 300°C for this study). Further, the minimum solubility given by Sweeton and Baes is found to be high by more than an order of magnitude.

If these proposed corrections to the Sweeton and Baes data are found to be justified, then many published papers which have used this data will need to be reviewed and some may need

to be revised. The next section of this report presents some AECL-sponsored experimental measurements of magnetite solubility which tend to support Tremaine's data rather than that of Sweeton and Baes.

Activity transport modellers have found good agreement between observations on reactors and predictions based on the Sweeton and Baes solubility data [8,31,32]. This correspondence cannot be ignored. If the true solubilities are unequivocally proven to be lower than formerly accepted, it may be necessary to invoke an "apparent solubility" or "equivalent solubility" concept, which takes into account very small particles and colloidal material. It may be that such matter is deposited on the surfaces of growing crystals and thereby precipitates as if it had been in solution. An experiment designed to test this concept might provide interesting results. Studies to date have ignored such considerations as the kinetics of dissolution and precipitation, and the actual removal processes which occur at the surfaces of the fuel elements. The intense radiation present in-core is likely to affect the local chemistry at the fuel surface. These, and other complicating factors, need to be understood in order to produce a truly meaningful model of activity transport around nuclear reactors.

### Experimental Studies

A radiochemical technique was developed for studying the dissolution of corrosion products (metal oxides) in high temperature water [33]. The technique is applicable to any sparingly soluble oxides, such as nickel ferrite and cobalt ferrite, but most of the work to date has been done with magnetite,  $Fe_3O_4$ . The apparatus consists essentially of three columns immersed in a constant temperature bath. The first and third columns are packed with inactive magnetite; the middle column is packed with irradiated (radioactive) magnetite (Figure 5).

The first column is used to presaturate the water which flows slowly through the system. Exchange between active and inactive ions in solution occurs in the second column, and active ions are adsorbed from solution onto the magnetite in the third column. The buildup of activity on the third column is followed with a Ge(Li) detector.

If the first column is left empty, the solubility of the irradiated oxide may be calculated; if the first (presaturating) column is full of oxide, then the kinetics of exchange may be

obtained. The last measure is the rate of solution of the oxide at equilibrium, when the concentration gradient driving force for dissolution has been removed. Results given by Balakrishnan [33] for the solubility of magnetite are significantly lower than those of Sweeton and Baes. Possible reasons for this are discussed in the original paper.

Balakrishnan's technique was used by researchers at the University of Manitoba to measure independently the solubility of magnetite in high temperature alkaline water [34]. Again, results obtained were lower than those reported by Sweeton and Baes. Further studies using this technique are in progress at Nova Scotia Research Foundation in Halifax, Nova Scotia, and Tremaine and co-workers at WNRE are measuring solubilities in H<sub>2</sub>O and D<sub>2</sub>O, using an apparatus similar to that used by Sweeton and Baes. In another year it is reasonable to expect more data from independent workers on the solubility of metal oxides at reactor temperatures and pH's, which should help resolve the validity of the Sweeton and Baes results.

#### 4. DECONTAMINATION

The rate of growth of radiation fields can be kept low by a judicious selection of materials of construction, by good control of coolant chemistry and by high purification flow to remove activated corrosion products or (preferably) corrosion products before they become active. Despite these measures the fields will inexorably grow, and will eventually reach a level when chemical decontamination is desirable.

Most decontamination processes have been developed with stainless steel in mind. They usually involve the addition of an alkaline oxidizing agent followed by relatively strong (6 to 10 wt%) concentration of organic acids. Such a process requires the primary coolant to be removed, and produces several reactor volumes of acidic, radioactive liquid waste. A detailed study by AECL of the application of one such process, APAC (alkaline permanganate followed by ammonia citrate) [35], indicated that several weeks of reactor shutdown would be needed to prepare the reactor, conduct the decontamination and restore the reactor to operating condition. Furthermore, it was expected that many (about 25%) of the mechanical seals used in the primary circuit would leak after such a decontamination. Fixing these leaks would involve a radiation dose to workers which would not have been necessary otherwise. Disposing of the large volume of active waste would also incur a radiation dose penalty. The

main advantage of the process was the high decontamination factor\* expected to result - a DF of at least ten was confidently expected.

Because of the disadvantages of APAC and other procedures considered, AECL attempted to devise a procedure in which relatively mild and dilute reagents could be added to the primary coolant itself, thus avoiding the downgrading or loss of expensive D<sub>2</sub>O and also the leaks caused by corrosion when using more concentrated and aggressive chemicals. It was accepted that a smaller DF would be achievable with milder reagents. Many commercial reagents and chemical mixtures were evaluated in AECL laboratories for decontamination efficiency and corrosiveness to the carbon steel primary circuit, nickel seal rings and high nickel alloy boiler tubes. A commercial mixture of organic acids and complexing agents was selected as giving an optimum balance between DF, corrosiveness and avoidance of redeposition of metals and oxides.

A means was then developed of regenerating on ion exchange resins the active ingredients of the mixture, so that the concentration present in the coolant at any time was dilute (about 0.1 wt%), thereby minimizing corrosion, and radioactive metallic ions were retained on the ion exchange beds, for which handling and disposal techniques were already available at the station.

A dilute, continuous process has the added advantage of being easily monitored (by corrosion monitors, pH meters and radiation counters) and controlled (by flow rates, temperature, addition of supplementary chemicals and removal of reagents on different ion exchange resins). This process is called CAN-DECON (CANdu DECONTamination). The concept of in situ removal of radioactive metallic ions and regeneration of the reagent is applicable to many reagents, not just the ones on which the development work was done.

Large-scale development trials of CAN-DECON were performed at NPD\*\* and Gentilly-1\*\*\* reactors, leading to a full-

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- \* Decontamination factor,  $DF = (\text{radiation field before decontamination}) / (\text{radiation field after decontamination})$
- \*\* NPD - Nuclear Power Demonstration, a 25 MWe CANDU-PHW reactor located at Rolphton, Ontario
- \*\*\* Gentilly-1 - a 250 MWe CANDU Boiling Light Water cooled reactor located at Gentilly, Quebec

scale CAN-DECON decontamination of Douglas Point\* in August 1975. A full account of this decontamination has been given elsewhere [36]. Only the highlights will be noted here.

A DF of 2 on the carbon steel feeder pipes was the primary objective. The main results, which are extremely gratifying to all concerned, were as follows:

- (a) The radiation fields on the feeder pipes were reduced from a range of 2 to 3 R/h to 0.3 to 0.5 R/h, with an average DF of 6.
- (b) Approximately 230 Ci (8.5 TBq) of Co-60 was removed from the system.
- (c) The leak rate of D<sub>2</sub>O from the primary circuit after decontamination was no greater than before decontamination.
- (d) Less than 10 rem were expended in performing the decontamination.
- (e) Comparing the actual rem expenditures for maintenance work at the subsequent shutdown with what would have been expended without the decontamination showed a net saving of 172 rem.
- (f) The actual time from reactor shutdown to start the decontamination until the reactor was in a condition to start up again was 72 h.

In the 3 years following the decontamination (August 1975 to August 1978) no deleterious consequences on reactor operation have been detected.

Because CAN-DECON is conducted with the fuel in place in the core, some radioactive corrosion products are removed before they have been redistributed out-of-core. This feature should reduce the rate of growth of fields after the decontamination, conferring a longer-term hidden benefit in dose reduction. In fact, the rate of growth of radiation fields around the boilers in the Douglas Point reactor has been virtually zero since the decontamination (Figure 6).

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\* Douglas Point - a 200 MWe CANDU-PHW reactor located at Kincardine, Ontario

DFs achieved by CAN-DECON are less than those obtainable with more aggressive decontamination methods but it is quick, cheap and easy to perform and relatively less corrosive. These features suggest that it could be applied more frequently, before fields become so high that an aggressive decontamination is required. Figure 7 compares the application of a strong decontaminant to reduce the fields to zero every seven years, with the use of CAN-DECON giving an average DF of three every 1 1/2 years. Other values may be used for this comparison, but, in general, frequent small DFs seem preferable to infrequent large DFs.

Although CAN-DECON was developed for CANDU reactors which have carbon steel primary circuits, the principle of using dilute, regenerable decontaminants is applicable to light water reactors with stainless steel circuits. Considerable interest in this process has been shown by light water reactor operators around the world. Accordingly, AECL have licensed a Canadian engineering company, W.P. London and Associates Limited, and their subsidiary company, London Nuclear Decontamination Limited, to develop and apply the AECL technology to all other systems for which it is deemed appropriate.

## 5. STEAM GENERATOR CORROSION

Steam generator corrosion has been a major cause of unreliability in PWRs. A recent survey [37] finds that about 35% of operating reactors are affected in any given year, and that over 80% of reactors that have exceeded 1000 Effective Full Power Days of operation have had tube failures. Most failures have been caused by corrosion, and the most severe corrosion has occurred at stations where the turbine condensate is cooled with sea-water. Sea-water salts (notably sodium and magnesium chlorides) enter the boiler feedwater through leaks in the condenser. The salts become concentrated within the bulk of the water in the boiler, and especially within crevices between the boiler tubes and their support plates. The several forms of corrosion which have resulted have been described and discussed extensively in the open literature [38]. CANDU-PHW reactors have been almost free from boiler problems [39,40]. In order to maintain that situation in the future, AECL have conducted extensive theoretical and experimental programs into boiler water chemistry and boiler tube corrosion.

### Theoretical Studies

A major contribution to the understanding of boiler tube corrosion is a theoretical prediction of the corrosiveness of various cooling waters when concentrated in the bulk boiler water and in heated crevices [41]. In this study, all the dissociation and hydrolysis reactions of the salts found in natural waters are assessed by computer. The computer program identifies the species that precipitate from a given solution when concentrated by boiling, and estimates the composition of the remaining solution.

Arbitrary operating conditions can be put into the program allowing studies to be made of the effects on the compositions of boiler water and of precipitates of different rates of blowdown from the boiler, or different boil off rates from and leakage rates into a crevice. Different compositions of condenser cooling water and different leakage rates through the condenser into the boiler feed water may also be studied. Some predictions from this study so far are:

- most fresh waters (e.g. the Great Lakes, the St. Lawrence River) produce alkaline solutions on concentration within a boiler,
- sea-water and brackish waters produce acidic solutions under similar conditions,
- the rate of blowdown of boiler water or rate of ingress into a crevice affect the time taken to establish steady state conditions, but not the composition of the final concentrated solution,
- the time to reach steady state conditions is short (hours or a few days, depending on operating parameters) compared with the operating time of power reactors, so that the rate of blowdown has little or no practical effect on boiler water chemistry, in the bulk or in crevices,
- silica ( $\text{SiO}_2$ ) added to boiler feedwater depresses the pH of the concentrated solution slightly, and modifies the composition of the precipitates, but does not radically change the aggressiveness of a water.



These theoretical studies are being expanded to include the effects of boiler water additives (amines, phosphates) on the corrosiveness of concentrated solutions formed in crevices. Also, experiments are starting to measure the compositions and rates of growth of concentrates in bulk boiling water and crevices, so as to evaluate directly the reliability of the theoretical predictions. The results of these experiments will be reported.

### Experimental Studies

The precipitation of salts from evaporating solutions of sodium phosphates has been studied and reported by others [42]. Our results are generally in agreement with published data. A useful contribution [43] from our work is a novel technique for isolating the solid formed at high temperature, avoiding the changes in composition which could occur as a mixed liquid/solid system is cooled down. In this device (Figure 8), a heated boiler tube is surrounded by a fine mesh stainless steel gauze. The test section is built into a water loop. During operation, solid is trapped between the boiler tube and the gauze. At the conclusion of the experiment the test section is isolated and the liquid phase blown off while still at test temperature, leaving the unchanged solid behind in the dry test section, which is then quickly cooled to room temperature. Experiments in this apparatus demonstrated the important role played by reactions between phosphate and magnetite in the hide-out of phosphate in an operating boiler.

## 6. AUTOMATIC CONTROL OF FEEDWATER CHEMISTRY

The common corrosion phenomena on PWR boiler tubes - caustic cracking, acid wastage, denting - have all been attributed to inadequate control of the boiler water chemistry. Much effort in AECL has been devoted to understanding these corrosion phenomena and defining the parameters which control their rates [44,45,46]. A primary concern is to ensure that aggressive cooling waters are prevented from entering the boiler feedwater. A novel design of condenser has been adopted to assist the achievement of this aim [47].

As an additional safeguard an automatic, computer controlled system of chemical analysis, interpretation and response has been developed [48], so that corrections may be made to the boiler water and feed water chemistry as soon as their composition departs from the approved specification (Figure 9).

Samples are taken regularly and automatically from various locations in the condenser, feedtrain and boiler blowdown. Preprogrammed analyses are made and the results transmitted as electrical signals to a dedicated computer. Each analytical cycle includes standard samples of different concentrations so that the responses of the instruments are checked regularly. If an out-of-specification signal is received the computer first calls for a special check with the standard solution. For important analyses, duplicate analyzers are provided. Having confirmed that the signal is valid, the computer initiates corrective action as well as providing alarm signals for the operators.

The components of the system were developed and checked independently and in small assemblies. Then the complete system was installed on a coal-fired power station of Saskatchewan Power Corporation for exhaustive testing and demonstration of long-time reliability. The development model is now about to be installed on a large model boiler experiment at a power station of New Brunswick Electric Power Commission, prior to installing a commercial version on the Point Lepreau CANDU-PHW reactor, which is currently under construction.

## 7. CONCLUDING COMMENTS

In this paper several experimental techniques and theoretical studies associated with the water chemistry circuits of CANDU-PHW reactors have been briefly discussed. A common theme connects the approach to each of these studies.

First, an attempt is made to develop a good understanding of the chemical processes to be controlled. This axiom is adhered to in all our studies, whether they are on activity transport, boiler water chemistry, reactivity control by soluble poisons, or any other process.

Based on the conclusions of the fundamental studies, actions are taken which are sometimes novel and which may not be the same as the actions dictated by ad hoc empirical observations. Because of this approach and the unique requirements of the CANDU concept, we often find ourselves at odds with the rest of the nuclear industry. Some examples of unique design in CANDU reactors which affect (and are affected by) considerations of chemistry and corrosion are:

- natural uranium fuel and D<sub>2</sub>O coolant,
- collapsible fuel cladding,
- pressure tubes,
- carbon steel primary circuit,

- Monel-400 boiler tubes,
- Incoloy-800 (Sanicro-30) boiler tubes,
- adherence to phosphate additions to counter sea-water leakage.

To support these concepts and maintain the reliability already demonstrated by operating CANDU reactors, a continuing program is maintained on chemistry and the properties of materials. Because of the open policy of publication within AECL we have developed very valuable relationships with scientists of other organizations around the world. This free interchange of ideas and constructive criticism has been beneficial to the CANDU program. We hope that our efforts have been of assistance to others.

## 7. REFERENCES

1. J.E. LeSurf, "The Water Chemistry of CANDU-PHW Reactors". Proc. of the BNES Intl. Conf. on the Water Chemistry of Nuclear Reactor Systems, Bournemouth, UK, Paper 19, 177-186 (1977 Oct. 24-27).
2. D.H. Lister, "The Mechanisms of Corrosion Product Transport and their Investigation in High-Temperature Water Loops". Paper 153 at the NACE CORROSION/78 Conf., Houston, Texas (1978 March).
3. D.H. Lister, "Predicting Radiation Fields Around Reactor Components". Canadian Nuclear Association Annual Conf. (1976 June). Session on Control of Reactor Radiation Fields (Vol. 8 of Conf. Proc.). Available as Atomic Energy of Canada Limited Report No. AECL-5522.
4. J.E. LeSurf, "Control of Radiation Exposures at CANDU Nuclear Power Stations". J. British Nuclear Energy Soc. 16, No. 1, 53-61 (1977 Jan).
5. K.A. Burrill, "Corrosion Product Transport in Water-Cooled Nuclear Reactors -  
"Part I - Pressurized Water Operation". Canadian J. of Chemical Engineering", 55, 54-61 (1977 Feb).  
"Part II - Boiling Water with Direct Cycle Operation". Ibid, 56, 79-86 (1978 Feb).  
"Part III - Boiling Water with Indirect Cycle Operation". Ibid. Submitted for publication.
6. K.A. Burrill, "A Possible Mechanism for Corrosion Product Transport and Radiation Field Growth in a Pressurized Water Reactor Primary Circuit". Nuclear Technology, 36, 85 (1977 Nov).
7. K.A. Burrill, "Corrosion Product Deposition and Release at Nuclear Fuel Sheaths in Boiling Water". Paper 154 at the NACE Annual Conference CORROSION/78, Houston, Texas (1978 March).
8. K.A. Burrill, "An Experimental Study to Link Water Chemistry with Corrosion Product Deposits In-Reactors". Proc. of the BNES Intl. Conf. on the Water Chemistry of Nuclear Reactor Systems, Bournemouth, (UK, Paper 13, 119-132 (1977 Oct)).

9. D.H. Lister, "The Transport of Radioactive Corrosion Products in High Temperature Water. Part I - Recirculating Loop Experiments". Nuclear Science & Engineering, 58, 239 (1975).
10. D.H. Lister, "The Transport of Radioactive Corrosion Products in High Temperature Water. Part II - The Activation of Isothermal Steel Surfaces". Nuclear Science & Engineering, 59, 406 (1976).
11. D.H. Lister, "Mass Transfer in the Contamination of Isothermal Steel Surfaces". Nuclear Science & Engineering, 61, 107 (1976).
12. P.V. Balakrishnan and G.M. Allison, "Some In-reactor Loop Experiments on Corrosion Product Transport and Water Chemistry". Nuclear Technology, 39, 105 (1978).
13. P.W. Tewari and A.B. Campbell, "The Surface Charges of Oxides and Their Role in Deposition and Radioactivity Transport in Water Cooled Reactors". Proc. of Symposium on Oxide-Electrolyte Interfaces, Electrochem. Soc., R.S. Alwitt, Editor (1973).
14. P.H. Tewari, R.H. Tuxworth and W. Lee, "Specific Adsorption of Co(II) by  $ZrO_2$  and  $Fe_2O_3$ ". Ibid.
15. P.H. Tewari and A.B. Campbell, "Temperature Dependence of Point of Zero Charge of Cobalt and Nickel Oxides and Hydroxides". J. Colloid and Interface Sci., 55, 531 (1976).
16. P.H. Tewari and W. Lee, "Adsorption of Co(II) at the Oxide-Water Interface". J. Colloid and Interface Sci., 52, 77 (1975).
17. D.D. Macdonald and T.E. Rummery, "The Growth of Iron Oxide Films on Carbon Steel and Platinum Surfaces in LiOH and NaOH Solutions at 285°C", Corrosion Sci., 15, 521 (1975).
18. T.E. Rummery and D.D. Macdonald, "Prediction of Corrosion Product Stability in High Temperature Aqueous Systems", J. Nucl. Mat., 55, 23 (1975).
19. D.D. Macdonald, G.R. Shierman and P. Butler, "The Thermodynamics of Metal-Water Systems at Elevated Temperatures. Part 1: The Water and Copper-Water Systems", Atomic Energy of Canada Limited Report No. AECL-4136 (1972).
20. Ibid., "Part 2: The Iron-Water System", Atomic Energy of Canada Limited Report No. AECL-4137 (1972).

21. Ibid., "Part 3: The Cobalt-Water System". Atomic Energy of Canada Limited Report No. AECL-4138 (1972).
22. D.D. Macdonald, "Part 4: The Nickel-Water System". Atomic Energy of Canada Limited Report No. AECL-4139 (1972).
23. D.D. Macdonald and T.E. Rummery, "The Thermodynamics of Metal Oxides in Water-Cooled Nuclear Reactors". Atomic Energy of Canada Limited Report No. AECL-4140 (1973).
24. T.E. Rummery and D.D. Macdonald, "The Thermodynamics of Selected Transition Metal Ferrites in High Temperature Aqueous Systems". Atomic Energy of Canada Limited Report No. AECL-4577 (1973).
25. D.D. Macdonald, T.E. Rummery and M. Tomlinson, "Stability and Solubility of Metal Oxides in High-Temperature Water". Thermodynamics of Nuclear Materials 1974, Vol. 11, IAEA-SM-190/19, 123-141 (1975).
26. R.E. Von Massow, G.R. Sullivan and G.N. Waugh, "Solubility of Nickel and Cobalt Ferrite in Water up to 300°C". Atomic Energy of Canada Limited Report No. AECL-4582 (1975).
27. P.R. Tremaine, T.E. Rummery and R.E. Von Massow, "Corrosion Product Stability in High Temperature Aqueous Systems - Deuterium Isotope Effects". J. Nucl. Mat., 68, 351-354 (1977).
28. P.R. Tremaine, R.E. Von Massow and G.R. Sherman, "A Calculation of Gibbs Free Energies for Ferrous Ions and the Solubility of Magnetite in H<sub>2</sub>O and D<sub>2</sub>O to 300°C". Thermochemica Acta, 19, 287-300 (1977).
29. C.M. Criss and J.W. Cobble, "The Thermodynamic Properties of High Temperature Aqueous Solutions -  
"IV - Entropies of the Ions Up to 200°C and the Correspondence Principle". J. Am. Chem. Soc., 86, 5385-5390 (1964).  
"V - The Calculation of Ionic Heat Capacities up to 200°C Entropies and Heat Capacities Above 200°C". Ibid, 86, 5390-5393 (1964).
30. F.H. Sweeton and C.F. Baes, Jr., "The Solubility of Magnetite and Hydrolysis of Ferrous Iron in Aqueous Solutions at Elevated Temperatures". J. Chem. Thermodynamics, 2, 479-500 (1970).

31. P. Beslu, G. Frejaville and A. Lalet, "A Computer Code PACTOLE to Predict Activation and Transport of Corrosion Products in a FWR". Proc. of the BNES Intl. Conf. on the Water Chemistry of Nuclear Reactor Systems, Bournemouth, UK, Paper 21, 195-202 (1977 Oct).
32. D.H. Lister, "The Growth of Radiation Fields Around CANDU Boilers". Ibid., Paper 23, 207-214.
33. P.V. Balakrishnan, "A Radiochemical Technique for the Study of Dissolution of Corrosion Products in High Temperature Water". Canadian J. of Chemical Engineering, 55, 357-360 (1977 June).
34. G.A. Kanert, G.W. Gray and W.G. Baldwin, "The Solubility of Magnetite in Basic Solutions at Elevated Temperatures". Atomic Energy of Canada Limited Report No. AECL-5528 (1976 Dec).
35. J.A. Ayres, Editor, "Decontamination of Nuclear Reactors and Equipment". The Ronald Press Co., New York (1970).
36. P.J. Pettit, J.E. LeSurf, W.B. Stewart and S.B. Vaughan, "Decontamination of the Douglas Point Reactor by the CAN-DECON Process". Paper No. 39 at the NACE Annual Conference CORROSION/78, Houston, Texas (1978 March). Submitted for publication in CORROSION Journal.
37. O.S. Tatone and R.S. Pathania, "Experience with Steam Generator Tubes in Water Cooled Nuclear Power Plants". Nucl. Eng. Intl., 23, No. 270, 35-39 (1978 April).
38. D.D. Malinowski and W.D. Fletcher, "Update of Operations with Westinghouse Steam Generators". Paper presented at The American Nuclear Society 23rd Annual Meeting, New York (1977 June).
39. R.I. Hodge, J.E. LeSurf and J.W. Hilborn, "Steam Generator Reliability - the Canadian Approach". Presented at the XIX Nuclear Congress of Rome, Italy (1974 March).
40. R.I. Hodge, J.E. LeSurf and J.W. Hilborn, "Steam Generator Reliability - Canadian Practice". Presented at the IAEA Intl. Symposium on Application of Reliability Technology to Nuclear Power Plants, Paper No. IAEA-SM-218/25, Vienna, Austria (1977 Oct.).

41. P.V. Balakrishnan, "Effect of Condenser Water In-leakage on Steam Generator Water Chemistry". Presented at the 38th Annual Meeting of the Intl. Water Conf., Pittsburgh, Penn., Paper No. IWC-77-12 (1977 Nov).
42. G. Economy, A.J. Panson, C.-T. Liu, J.N. Esposito and W.T. Lindsay, Jr., "Sodium Phosphate Solutions at Boiler Conditions - Solubility, Phase Equilibria and Interactions with Magnetite". Proc. 36th Intl. Water Conf., Pittsburg, Penn. (1975 Nov).
43. P.V. Balakrishnan, "A Study of Phosphate Hide-Out from Boiling Water". Canadian J. of Chemical Engineering, 55, 592-596 (1977 Oct).
44. P.V. Balakrishnan and E.G. McVey, "Model Boiler Studies on Deposition and Corrosion". Presented at the NACE Canadian Eastern Regional Conf. on Corrosion in the Power Industry, Montreal, Quebec, 1977 Sept. Available as Atomic Energy of Canada Limited Report No. AECL-5801.
45. R.S. Pathania and J.A. Chitty, "Stress Corrosion Cracking of Steam Generator Tube Materials in Sodium Hydroxide Solution". Paper 198 at the NACE Annual Conf. CORROSION/78, Houston, Texas (1978 March). Accepted for publication in CORROSION Journal.
46. R.S. Pathania, "The Effect of Cooling Water Leakage on Corrosion of Steam Generator Materials". To be presented at the NACE Annual Conf. CORROSION/79, Atlanta, Georgia, 1979 March. To be submitted to CORROSION Journal.
47. G.F. Taylor, "Heat Exchanger Tubing Materials for CANDU Nuclear Generating Stations". Presented at the 22nd Nuclear Congress of Rome, Italy (1977 March). Atomic Energy of Canada Limited Report No. AECL-5832.
48. J.R. Dean and R.B. Stewart, "Development of an Automated System for CANDU Secondary Coolant Circuit Chemistry Control". Atomic Energy of Canada Limited Report No. AECL-5997 (April 1978).



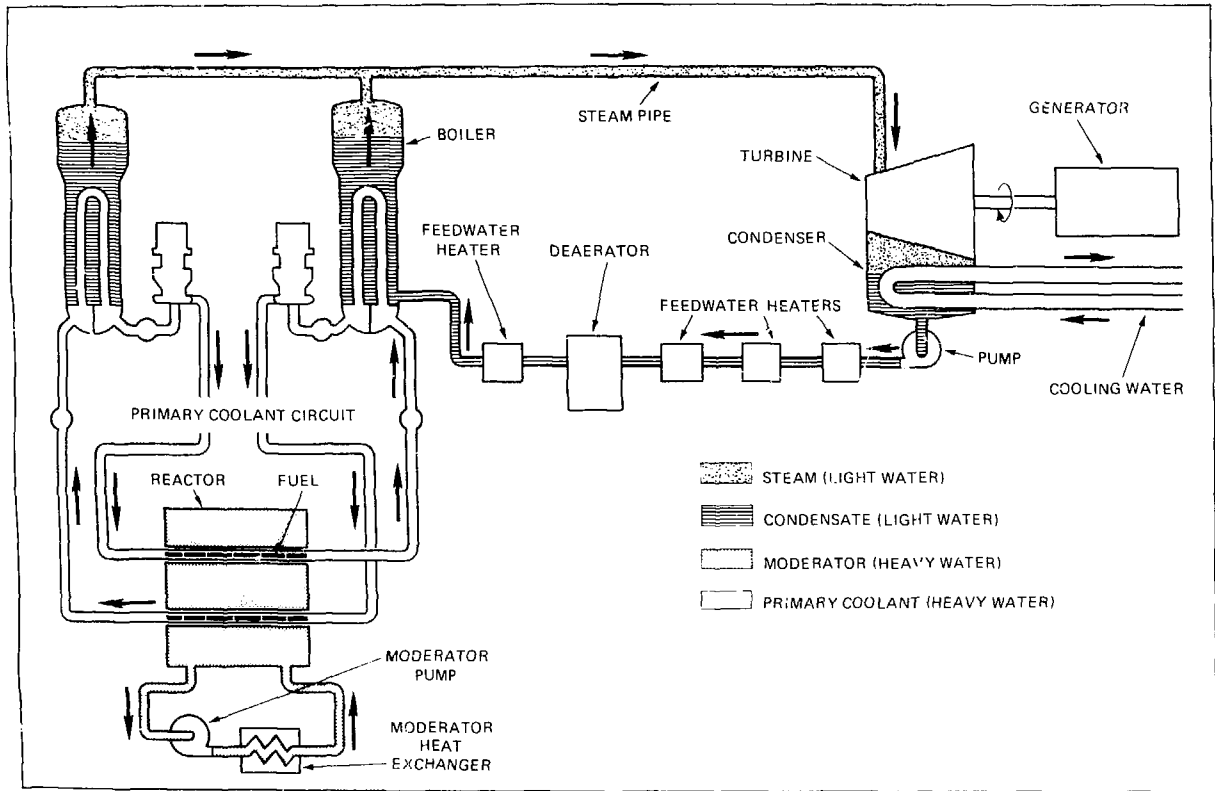


FIGURE 1 WATER CIRCUITS OF A PRESSURIZED HEAVY WATER REACTOR (CANDU-PHW)

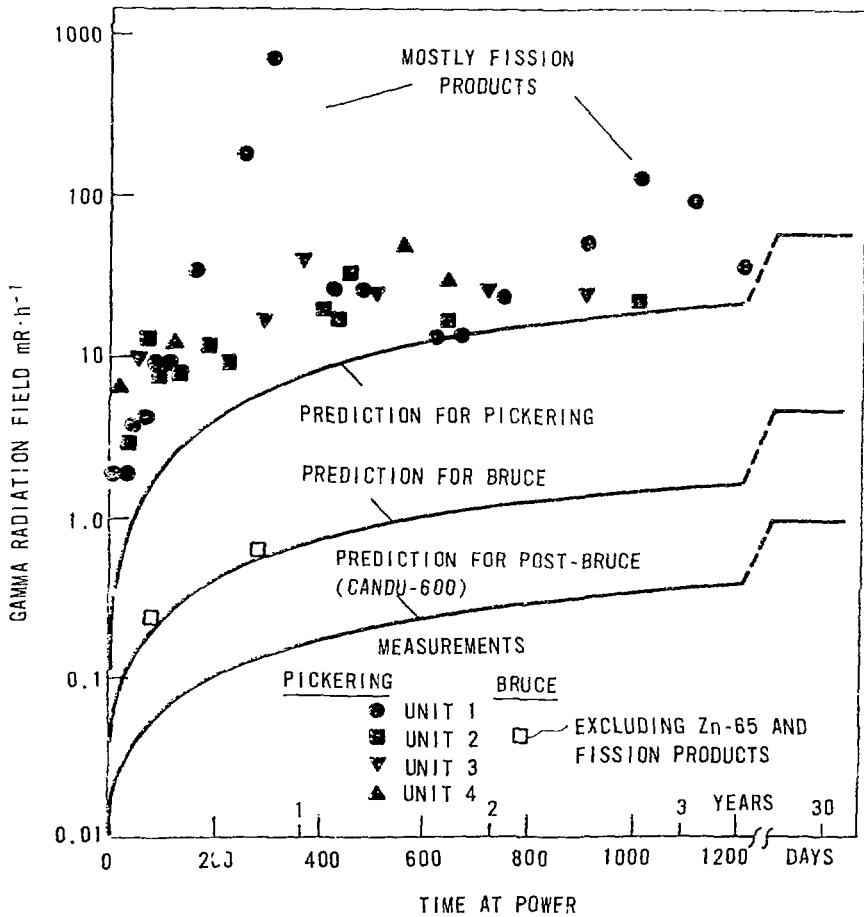


FIGURE 2 BOILER FIELD PREDICTIONS

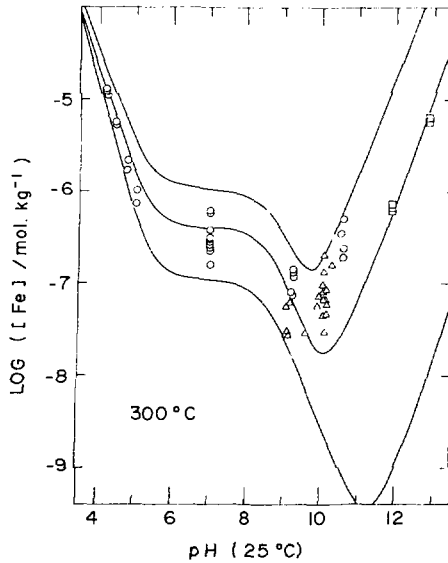


FIGURE 3 EXPERIMENTAL AND CALCULATED SOLUBILITIES OF MAGNETITE IN  $H_2O$  AT  $300^\circ C$  PLOTTED AGAINST THE pH OF THE HYDROGEN SATURATED FEED SOLUTION AT  $25^\circ C$ . THE UPPER AND LOWER CURVES ARE THE MAXIMUM AND MINIMUM CALCULATED SOLUBILITIES. THE MIDDLE CURVE IS FITTED TO THE DATA. (Ref. 28)

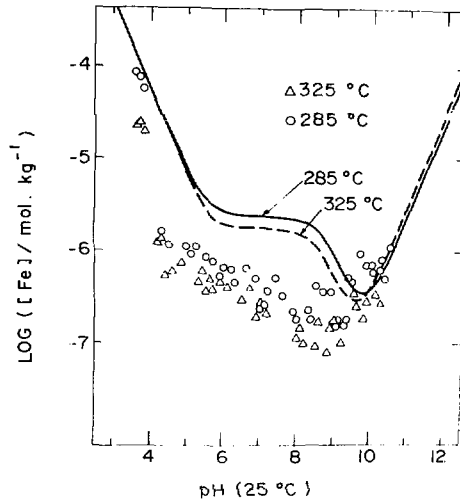


FIGURE 4 EXPERIMENTAL AND CALCULATED SOLUBILITIES OF MAGNETITE IN  $H_2O$  AT  $285^\circ C$  WITH  $7.01 \text{ MPa } H_2$  AND AT  $325^\circ C$  WITH  $12.6 \text{ MPa } H_2$ . (Ref. 28)

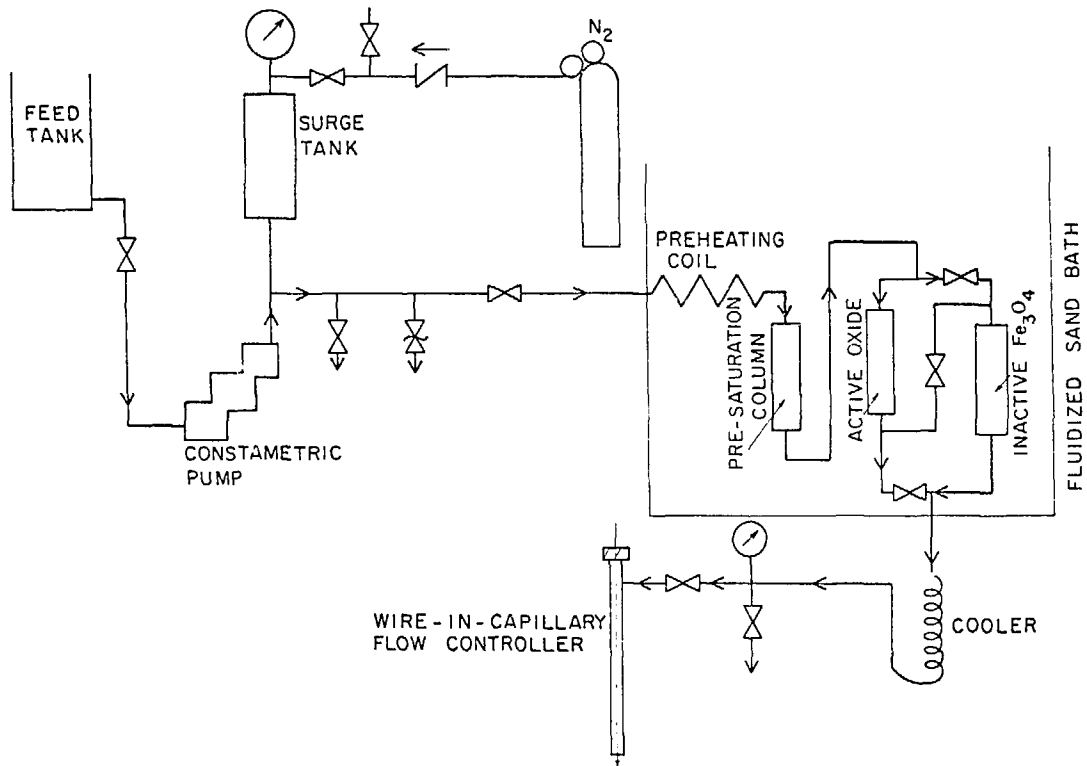


FIGURE 5 FLOW DIAGRAM OF THE EXPERIMENTAL SYSTEM FOR MEASUREMENT OF SOLUBILITY AND DISSOLUTION RATE (Ref. 33)

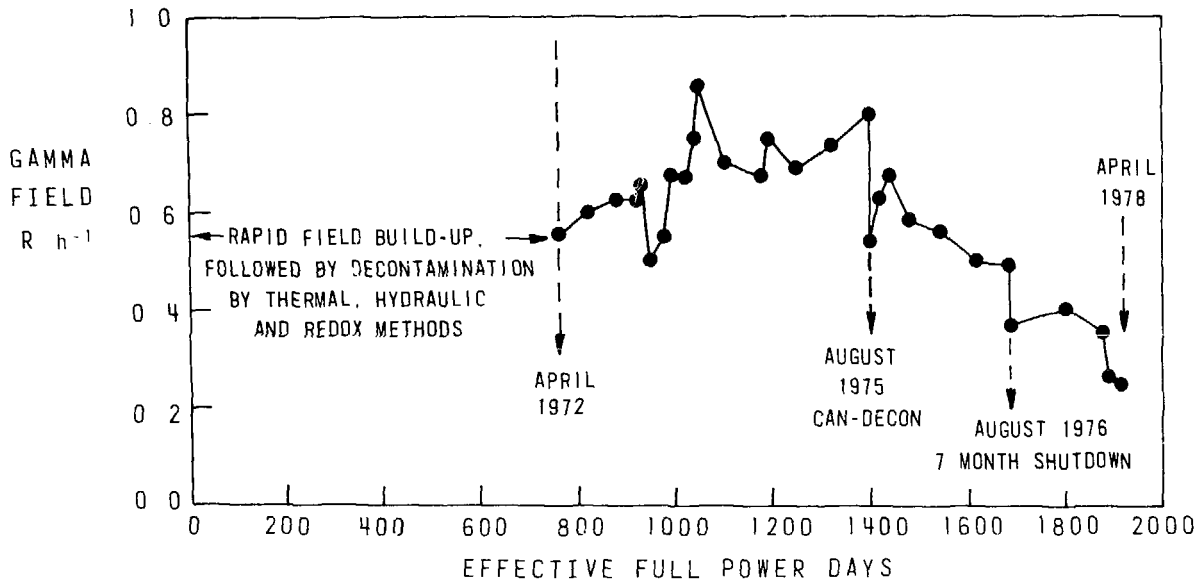


FIGURE 6 BOILER ROOM FIELDS AT DOUGLAS POINT N G S  
(AVERAGE OF 8 BOILER CABINET SIDES, MEASURED 24h AFTER SHUTDOWN)

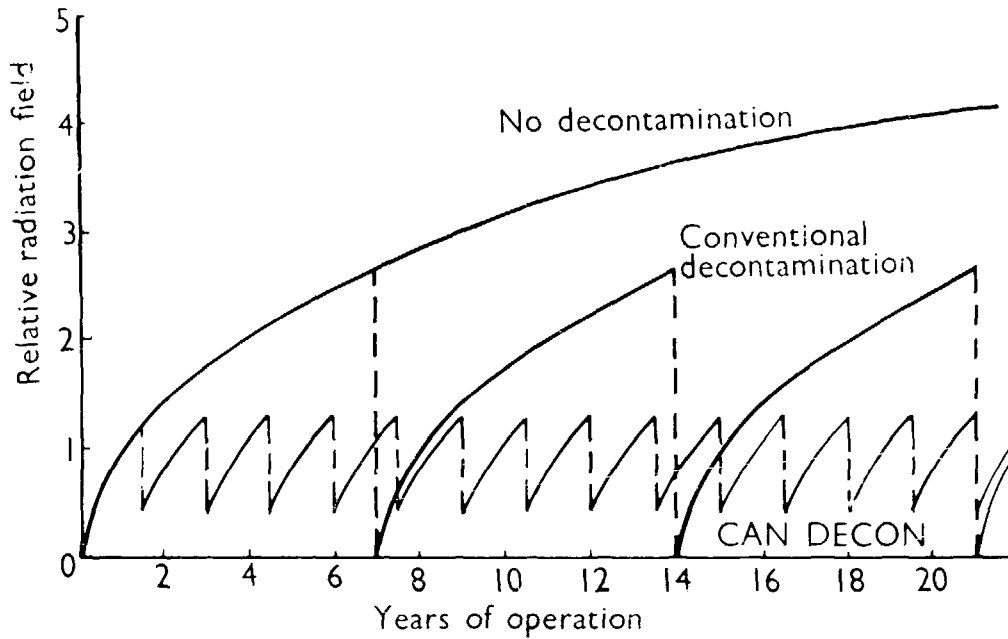


FIGURE 7 EFFECT ON RADIATION FIELDS OF PERIODIC DECONTAMINATION

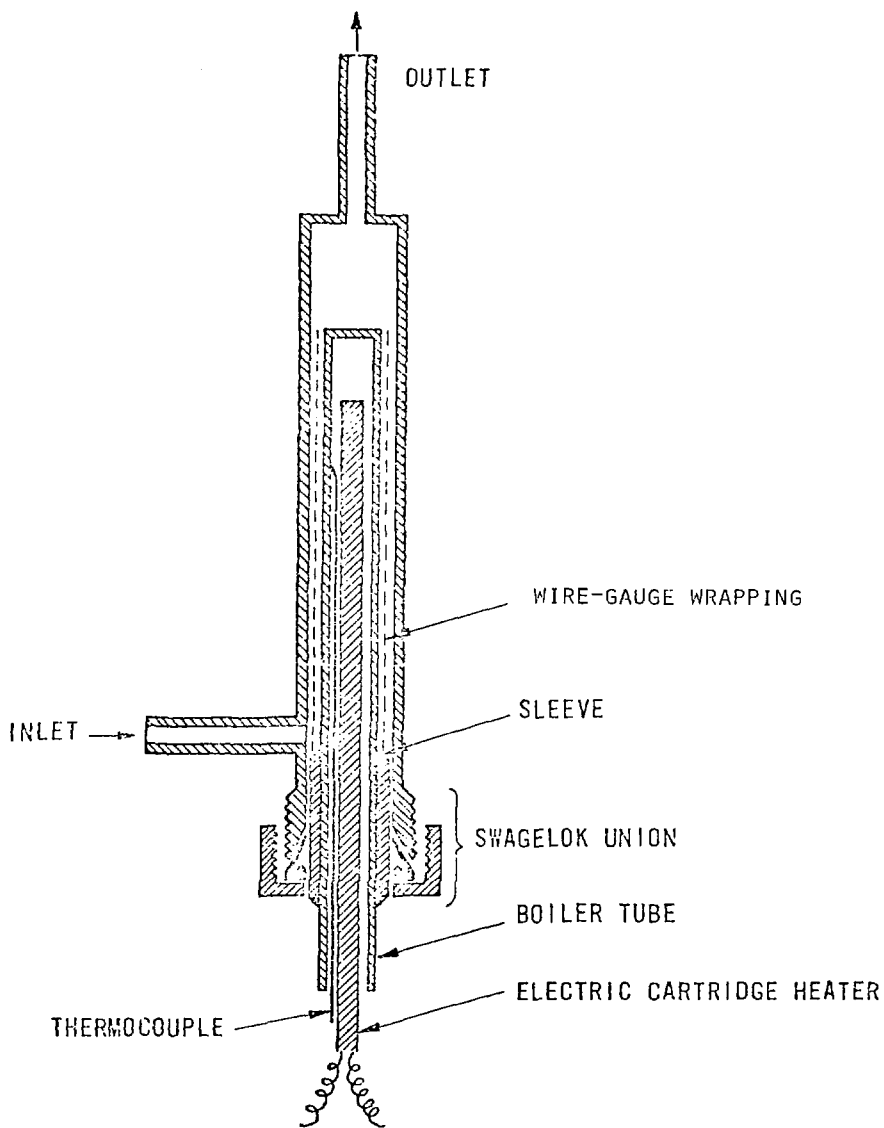


FIGURE 8 TEST SECTION OF AN APPARATUS TO STUDY THE DEPOSITION OF SOLIDS FROM BOILER WATER (Ref. 43)

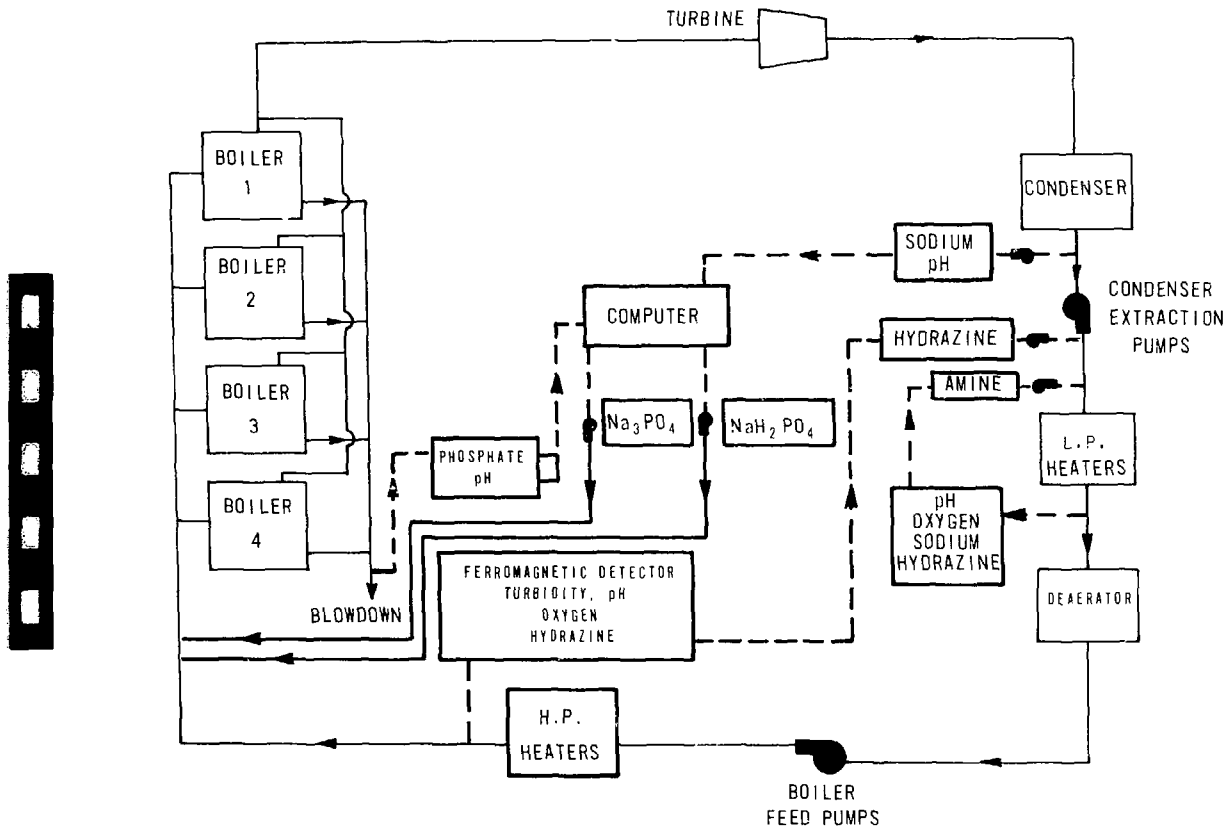


FIGURE 9 SCHEMATIC OF AUTOMATIC CHEMISTRY CONTROL SYSTEM PROPOSED FOR A CANDU 600 STEAM GENERATOR (Ref. 48)



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