



## PREVENTION OF ORGANIC IODIDE FORMATION IN BWR'S

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### Abstract

During an accident, many different forms of iodine may emerge. Organic iodides, such as methyl iodide and ethyl iodide, are relatively volatile, and thus their appearance leads to increased concentration of gaseous iodine. Since organic iodides are also relatively immune to most accident mitigation measures, such as sprays and filters, they can affect the accident source term significantly even when only a small portion of iodine is in organic form.

Formation of organic iodides may not be limited by the amount of organic substances available. Excessive amounts of methane can be produced, for example, during oxidation of boron carbide, which is used in BWR's as a neutron absorber material. Another important source is cable insulation. In a BWR, a large quantity of cables is placed below the pressure vessel. Thus a large quantity of pyrolyse gases will be produced, should the vessel fail.

Organic iodides can be formed as a result of many different reactions, but at least in certain conditions the main reaction takes place between an organic radical produced by radiolysis and elemental iodine. A necessary requirement for prevention of organic iodide production is therefore that the pH in the containment water pools is kept high enough to eliminate formation of elemental iodine. In a typical BWR the suppression pool water is usually unbuffered. As a result, the pH may be dominated by chemicals introduced during an accident. If no system for adding basic chemicals is operable, the main factor affecting pool water pH may be hydrochloric acid released during cable degradation. Should this occur, the conditions could be very favorable for production of elemental iodine and, consequently, formation of organic iodides.

Although high pH is necessary for iodine retention, it could have also some adverse effects. High pH may, for example, accelerate corrosion of containment materials and alter the characteristics of the solid corrosion products.

A study has been initiated by Finnish Centre for Radiation and Nuclear Safety (STUK) aiming at measuring the corrosion rates of zinc and aluminum in conditions typical for BWR's. Also the corrosion product characteristics are to be analyzed. The study is ongoing, but the main results gained so far are presented here.

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## 1. INTRODUCTION

The potential for releases of iodine in the early phase of an accident is mostly dominated by the formation, transport and deposition of aerosol-borne radioiodine. A feature specific to BWR's is that most aerosols released into the containment either through the lines for pressure relief or a break are carried into a suppression pool, provided that the containment remains intact. Since the aerosols vented into a suppression pool are usually efficiently removed from the vent gas, the potential for late releases is inherently reduced. With the containment sprays operating the late release potential experiences further decrease. Would there be no other processes involved, the risk of late releases could be practically eliminated without any further actions. This, however, is not necessarily the case. Fission products deposited in the primary circuit may be revolatilized, if the primary is allowed to remain without cooling. Should this take place after the containment leaktightness is lost, the fission products leaving the primary may pass both suppression pool and sprays escaping directly into the environment. The potential for late releases may also be increased by iodine chemistry, since there are reactions which may lead to formation of volatile iodine species, such as elemental iodine and organic iodides, under unfavorable conditions.

In this paper, the production of volatile iodine, and organic iodides in particular, under severe accident conditions is discussed with specific reference to boiling water reactors.

It is well-known that a necessary requirement for eliminating volatile iodine production is to assure that the water solution containing iodine is basic ( $\text{pH} > 7$ ) [1]. Although high pH is beneficial for iodine retention, it may have also some adverse effects. Water pH affects for example corrosion of containment materials, such as zinc and aluminum. Since all previous studies on corrosion of zinc and aluminum were concentrated solely on estimating the hydrogen generation potential of these materials, while little or no concern was paid to the nature of the solid corrosion products, a new study was initiated by Finnish Centre for Radiation and Nuclear Safety (STUK). The purpose of this study was to measure the corrosion rates of zinc and aluminum in conditions relevant to BWR's and to characterize the solid corrosion products. The main results gained so far are presented here.

## 2. ACCIDENT MANAGEMENT IN BWR'S

All BWR's have containments equipped with so-called pressure suppression system. The containment consists basically of two parts: the drywell housing the pressure vessel and the wetwell containing a large volume of water. All excess steam pressurizing either the primary or the drywell is vented into the wetwell pool, called suppression pool, for condensation. The advantages of such pressure suppression system are that the size of the containment can be reduced and the need for maintenance is usually low.

The pressure suppression system has also some disadvantages. Since the containment is typically small, oxidation of zircaloy can produce so much hydrogen that detonations could be possible, were hydrogen allowed to mix with air. To avoid such conditions, most BWR containments (excluding Mark III type) are inerted during normal operation, i.e. the oxygen concentration is kept below 5 %.

Yet hydrogen may pressurize the containment even without burning. This is possible during a primary pipe rupture, when steam from the primary carries both nitrogen from the drywell and hydrogen produced in the core to the wetwell. The same conditions can be achieved also without pipe break, if the accident proceeds to pressure vessel failure. In order to avoid uncontrolled containment rupture due to packing of non-condensables, BWR containments are equipped with vent lines, which are usually connected to filters for fission product retention. Various different filtering designs, including charcoal filters and scrubbers, are used.

For controlling pressure and temperature in the drywell during an accident, most BWR's have containment sprays, which can also be used for washing fission products from the drywell gas phase. For this purpose, alkaline chemicals can be added into the spray water. Since the spray water flows down to the suppression pool, from where it is circulated back to the spray system, addition of chemicals into the spray water determines as well the pH in the suppression pool.

Suppression pool acts as a water reservoir also for emergency core cooling systems. Since boric acid is not used in BWR's for reactivity control during normal operation, there is no apparent need for strong buffering of the suppression pool water. Consequently, the pH level in the suppression pool water is relatively sensitive to the chemicals introduced during an accident. In this respect the situation is different from that of PWR's, where a large amount of alkaline chemicals has to be added into the sump water in order to compensate the presence of boric acid alone. In many PWR this is done passively with chemicals stored either in the ice condensers or in a storage near the sump level, where they will be inherently flooded during an accident.

### **3. FORMATION OF VOLATILE IODINE**

The behavior of iodine dissolved in the containment water pools depends on many factors including iodine concentration, temperature, pH, redox potential and the presence of impurities. A complete chemical analysis of iodine behavior is a very demanding task and clearly out of the scope of this paper. However, the essence of iodine chemistry from the accident management point of view can be captured by noticing that formation of volatile iodine requires acidic conditions, while in basic conditions nonvolatile forms prevail [1]. Consequently, it is of paramount importance that the high pH level is maintained throughout an accident. Due to the BWR characteristics, the pH control may be difficult to achieve in certain conditions. These conditions, together with the effects induced by the low pH level on volatile iodine formation, are discussed below.

#### **3.1 Challenges to pH control**

After iodine is released from the fuel, it will be transported to the suppression pool either through the vent lines leaving the primary or, as in the case of LOCA, through the lines leaving the drywell. It is therefore mainly the suppression pool, where iodine chemistry takes place.

Since the suppression pool is usually unbuffered, the chemicals introduced during an accident can have a large impact on the pH level, as illustrated with a simple example. A typical water

volume of a suppression pool is about 3500 m<sup>3</sup>. If the initial pH is assumed to be 8, there are about 4 mol of OH<sup>-</sup> ions present in the water. During an accident, mainly basic fission products, such as CsOH, may be released. The cesium inventory in the core is typically of the order of 200 kg. As CsOH, this would yield 1500 mol OH<sup>-</sup> ions in the suppression pool and, consequently, rise pH up to the value of 10.6. The same could be achieved by adding 25 l of LiOH into the spray water. If both took place, the pH would climb up near 11.

Also acidic materials may be introduced during an accident. For example, iodine can be released as hydriodic acid (HI), although in relatively small quantities. More significant could be formation of carbonic acid as a result of absorption of carbon dioxide released during a melt-concrete interaction. Also nitric acid could be produced by the irradiation of water and air. However, since these processes are relative slow, at least in the short run the main source of acids may be the cables in the drywell [2,3].

Due to the fact that there are steam separators on the top of the core in every BWR, the mechanisms for control rod driving have to be located below the pressure vessel. As a result, there is a large number of cables in the vicinity of the pressure vessel bottom. If the containment sprays are not operable or the pressure vessel fails, these cables will be heated. Should this occur, a large quantity of hydrochloric acid (HCl) would be produced together with pyrolyse gases [4]. A rough estimate on the amount of hydrochloric acid can be given assuming that the amount of insulation near the pressure vessel is 2000 - 4000 kg [2,3]. A common insulation material is Lipalon, which has about 5 mol of chlorine for each kilo of insulation [4]. Complete release of chlorine could thus cause a release of 10 000 - 20 000 mol of HCl. If not compensated, this would reduce pH in the suppression pool to 2.2 - 2.5. Such release is possible, if the cables are heated up to temperatures around 600°C or higher [3,4].

Also irradiation may release hydrochloric acid from the cables. Beahm with his co-workers have calculated the amounts of HCl generated due to radiolysis of Hypalon using best estimate radiation levels following a LOCA. They concluded that the fractional release of HCl could be from 5 to 15 % in 12 hours and from 9 to 25 % in 24 hours [2]. In our example case, irradiation would yield 500 - 3000 mol of HCl after 12 hours and 900 - 5000 mol after 24 hours, i.e. enough to superimpose the effects of basic fission products introduced during an accident.

Consequently, if the suppression pool water is let alone to remain unbuffered during an accident, the pH in the containment water may decrease with time to values low enough to permit formation of volatile iodine in all accident sequences involving considerable core damage. In order to prevent this, some measures are needed. If these measures are taken only after a reduction in the pH level has been observed, they may be difficult to execute, because working in environment with high radiation level may be required. Better solution at least from the iodine retention point of view would be either to increase the buffering capacity of the suppression pool or to design more robust or even passive systems for addition of chemicals during an accident.

The effects of cable degradation are not necessarily limited to the containment. If containment venting is applied with the vent lines beginning from the drywell, the acidic materials released during cable pyrolysis and radiolysis could be carried to the filters. Should this occur, a loss of filtering may follow with subsequent release of iodine retained prior to cable degradation.

### 3.2 Consequences of iodine volatilization

When the water pH is reduced to values below 7, formation of elemental iodine will start with a rate depended on temperature, dose rate, concentration and redox conditions. As elemental iodine is produced, part of it will remain in the water solution while some will become gaseous. The partition between different phases may occur in a relatively long time scale, but eventually a situation will be reached, in which the concentrations in the liquid and gas phase are in equilibrium.

As the partition coefficient (defined as a ratio between concentrations in the liquid and gas phase) for elemental iodine varies from 30 at 50°C to 5 at 100°C [2], the concentration of gaseous iodine increases with increasing temperature. With BWR's, the ratio of containment gas and water volumes is 2.5 - 3 (excluding Mark III type), and thus at most 40 % of elemental iodine would be gaseous at the temperature of 100°C, while at lower end of the temperature spectrum the amount would be less than 10 %. However, these values bound the amount of gaseous elemental iodine only in static conditions. When venting is started, the iodine concentration in the gas phase decreases disturbing the partition equilibrium and, consequently, more iodine is volatilized. If venting would be allowed to continue indefinitely, all elemental iodine dissolved in the water pools would be released.

If filters are applied, this alone may not be detrimental. However, some problems may be encountered, since the filters are not designed to cope with such iodine loads. For example, scrubbers may run dry earlier than anticipated resulting loss of filtering. If all water is evaporated, also some iodine retained prior to dry out would be released.

Another consequence of formation of elemental iodine is that it opens the way for organic iodides. While degradation of cables, either due heating or irradiation, tends to cause reduction in the pH level, it also produces gaseous hydrocarbons, such as methane. Under irradiation these compounds can be ionized to form free radicals, which may react with elemental iodine. This reaction can take place in the liquid phase, when the hydrocarbons are carried through the suppression pool, or in the wetwell gas phase, where all non-condensables will be packed, if the pressure in the drywell is not reduced by any means. Reactions in both phases have been shown to be very efficient at least in optimal conditions.

The reactions in the liquid phase have been studied by Beahm and his co-workers, who did experiments by bubbling a mixture of methane and argon through a iodine solution under irradiation. Different flow rates and pH levels were used. According to their results, more than 40 % of dissolved iodine can form methyl iodide under suitable conditions [5]. The effects of high-molecular-weight hydrocarbons or impurities such as chloride were not studied.

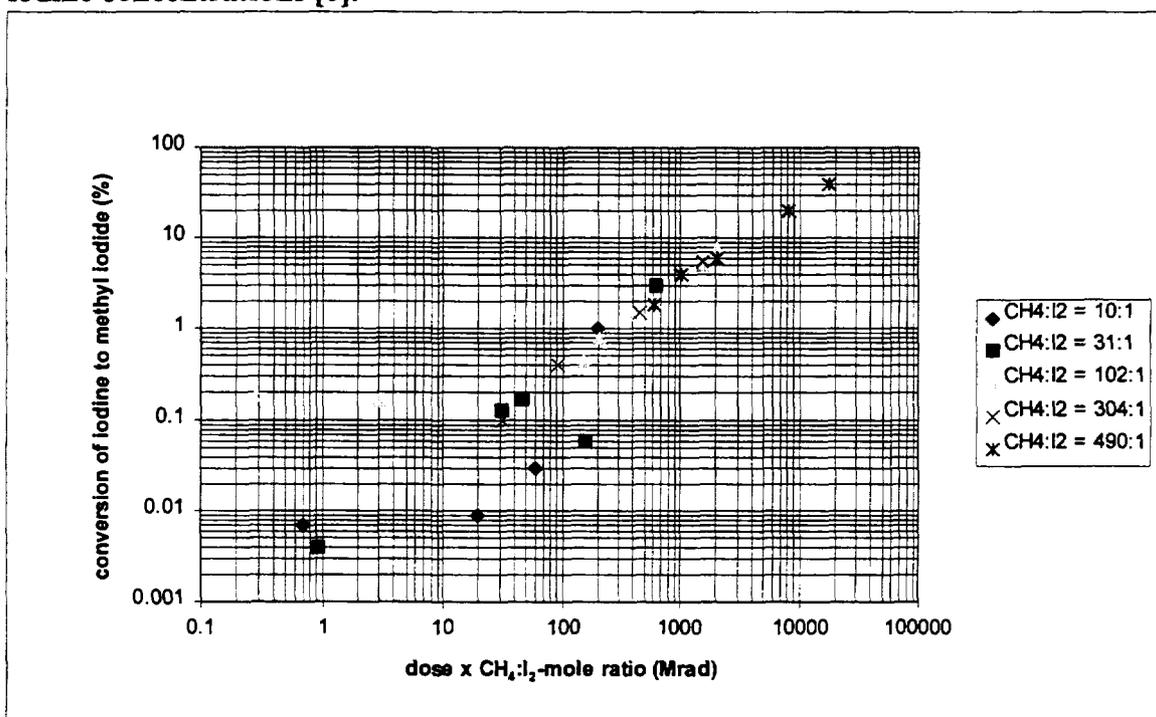
While the studies concerning reactions in the suppression pool are few, the gas phase reactions have been studied quite extensively, although usually in conditions most relevant to PWR's, i.e. with air present. Since oxygen is known to be an efficient free radical scavenger, it is not obvious that the results of these tests can be applied to BWR's, where the oxygen concentration may be much lower due to containment inerting and venting.

In a limiting case, when there is no oxygen in the gas phase, the formation of organic iodides appears to very efficient. In these conditions the reaction between iodine and methyl radicals

can be sustained to exhaustion of iodine with the rate of methyl iodide formation depending on the dose rate and the ratio between methane and iodine concentrations [6,7].

The time scale associated to formation of methyl iodide can be illustrated using the results of Kircher and Barnes [6]. They did tests using high methane and iodine concentrations of  $5 \cdot 10^{-3}$  -  $2 \cdot 10^{-2}$  and  $2 \cdot 10^{-5}$  -  $8 \cdot 10^{-5}$  mol/l, respectively, both in pure methane-iodine atmosphere and with steam present. The results of their tests without steam are presented in Figure 1 with the conversion ratio on the y-axis and the outcome of multiplication of the respective dose and the ratio of methyl and iodine concentrations on the x-axis.

**Fig. 1. Formation of methyl iodide as a function of dose and the ratio of methyl and iodine concentrations [6].**



For example, let us consider a situation in which 10 % of iodine is in the form of gaseous elemental iodine occupying a wetwell gas volume of  $3500 \text{ m}^3$ . The dose rate caused by iodine alone can be roughly estimated by using the dose rate conversion factors [8]. Six hours after the scram, the dose rate in the wetwell of  $1000 \text{ MW}_e$  plant would be 22 Mrad/h (assuming infinite medium). Together with all noble gases, the total rate would be around 35 Mrad/h. Assuming that the amount of methane present in the wetwell is equal to that of iodine, the dose needed to convert 10 % of gaseous iodine (i.e. 1 % of all iodine) into organic form would be around 4000 Mrad. With also steam present, the dose needed for the conversion would be even less, since the presence of steam has been found to accelerate conversion [6]. Should thus the dose rate be constant, less than 100 hours of irradiation would be needed for the conversion. However, since in practice the dose rate would decrease with time, the time required would be considerably longer.

Yet there may be also excess methane in the wetwell. The amount of methane can be estimated conservatively according to the results by Fridemo and Liljenzin [4]. They measured the amount of hydrocarbons released due to pyrolysis as a function of temperature. At the high end of the temperature range studied, i.e. near  $1000^\circ\text{C}$ , the amount of pyrolyse

gases was about 8 mol for each kilo of insulation. Assuming that the total amount of insulation is 2000 kg, this would yield 16 000 mol of pyrolyse gases, possibly even more if radiation effects are included. Were methane the only pyrolysis product, the ratio between methane and iodine concentrations could be as high as 3000:1. In these conditions, total conversion of gaseous iodine into methyl iodide would occur in half an hour. This is probably a very conservative estimate, but nevertheless illustrates the vast potential for organic iodide production at least in steam atmosphere, i.e. after venting.

It is obvious that the amount of hydrocarbons is very difficult to estimate with any certainty, since in practice also gases other than methane would be produced during pyrolysis. The task is made more difficult, when also oxidation of boron carbide, which is used in BWR's as a neutron absorber material, is included. During an accident, boron carbide may react chemically with steam. Several reactions are possible, but at least one of them includes methane as a final product. Should this reaction take place, less than 1 % of boron carbide in the core is needed to produce the amount equal to the iodine inventory. Presently these oxidation reactions are not very well known, and even less is known about reactions between methane and iodine in the primary circuit at high temperature. Consequently, considerable effort is needed in order to make the analysis more mechanistic.

The situation becomes even more complicated, when one considers formation of organic iodides before venting, when more substances are likely to be present. Some, as steam and possibly also hydrogen, may accelerate iodine conversion, as suggested by Kircher and Barnes, while others, notably oxygen, may have an opposite effect. It appears that complete conversion is no longer possible in these conditions. However, the amount of organic iodides could still be temporarily as high as 20 - 30 % of gaseous iodine, as observed in the tests simulating accident conditions in PWR plants [9].

It can be concluded that there seems to exist a considerable potential for organic iodide formation in BWR containment provided that elemental iodine is formed, i.e. the pH level in suppression pool is lowered during an accident. Organic iodides can be formed both in the liquid and gas phase. Quantitative estimates concerning the rate of organic iodide production can be made for the conditions prevailing after venting. If only steam, hydrocarbons and iodine are assumed to be present, relatively rapid conversion can occur leading to complete depletion of gaseous elemental iodine. If there is also oxygen in the atmosphere, the conversion of iodine may be restrained, but it is highly uncertain whether the oxygen levels typical for BWR's would be enough to suppress formation of organic iodides completely.

#### **4. POSSIBLY ADVERSE EFFECTS OF BASIC WATER CHEMISTRY**

Although basic water chemistry is clearly a necessity for iodine retention, it may effect accident mitigation and management also in other ways. For example, corrosion of containment materials, such as zinc and aluminum, depends heavily on the water chemistry.

Whether corrosion of zinc and aluminum will have any significant impact on accident management depends upon variety of factors, including the amount of and the characteristics of solid corrosion products. Although corrosion of zinc and aluminum has been studied quite extensively already in the past, the data available is not sufficient for assessment of both these

factors especially in conditions relevant to BWR's. Therefore a new study was initiated by the Finnish Centre for Radiation and Nuclear Safety (STUK).

#### 4.1 Experimental approach

The experiments were done by installing plates of galvanized steel and aluminum together with two metal wires, one made of zinc and the other made of aluminum, into a autoclave filled with deionized water. After installing the autoclave was pressurized and heated.

The corrosion rates of zinc and aluminum wires were determined by measuring *in line* their electrical resistances. As the oxidation of the metal wire and consequently the diminishing of cross-sectional area of the wire proceed the electrical resistance of the wire increases. The measured corrosion rates were compared with observed corrosion in the plates. The plates were weighed before and after each test. The post-test weight was measured before and after the dissolution of oxide layer.

In the first test series, both pressure and temperature were kept constant for a certain period, after which they were lowered step by step. The purpose of these tests was to simulate conditions during a LOCA. The main parameters in these tests were temperature and pH. Only lithiumhydroxide was used for adjusting pH. The temperatures used were 130, 110, 90, 70 and 50°C with corresponding pressures of 3.5 and 2.5 bars for the first two steps and 1.5 bars for the rest. The complete duration of each test was about 170 hours, with a duration of 6 and 24 hours for the steps at temperatures of 130 and 110°C, correspondingly. The steps at lower temperatures lasted about 48 hours each. Alternatively either nitrogen or air was continuously bubbled through the solution in order to assure efficient mixing.

The examination of solid corrosion products in the tests was limited to zinc. In order to obtain enough solid corrosion products for further analysis, a relatively large number of galvanized steel plates was used in each test.

In the second test series, the effect of hydrochloric acid was studied by making tests with uniform temperature of 50°C. pH was adjusted by adding lithium hydroxide to hydrochloric acid. Aerated water was used in these tests.

#### 4.2 The measured corrosion rates

The corrosion rates determined by means of the measured increase in the resistance of the corroding wires in the first test series are presented in Figures 2 and 3. The rates measured using this technique corresponded well with the observed weight loss results of aluminum and galvanized steel plates.

Validity of the experimental approach is supported also by earlier results, although tests suitable for such comparison are rare. For zinc, the only appropriate tests available are those with pure water at temperatures of 48 and 107°C [10]. The measured corrosion rates were 0.088 and 0.34 g/m<sup>2</sup>h, correspondingly, in full agreement with recent observations. For aluminum some test results are available also for BWR solutions. Fried et al. made tests with different aluminum alloys applying temperatures of 50, 100 and 150°C with pH either 5 or 9 [11]. In most tests corrosion rate was determined by weight measurements. In few tests also

Figure 2. Corrosion rates ( $\text{g/m}^2\text{h}$ ) for zinc as a function of pH and temperature, determined by means of the measured increase in the resistance of the corroding wires.

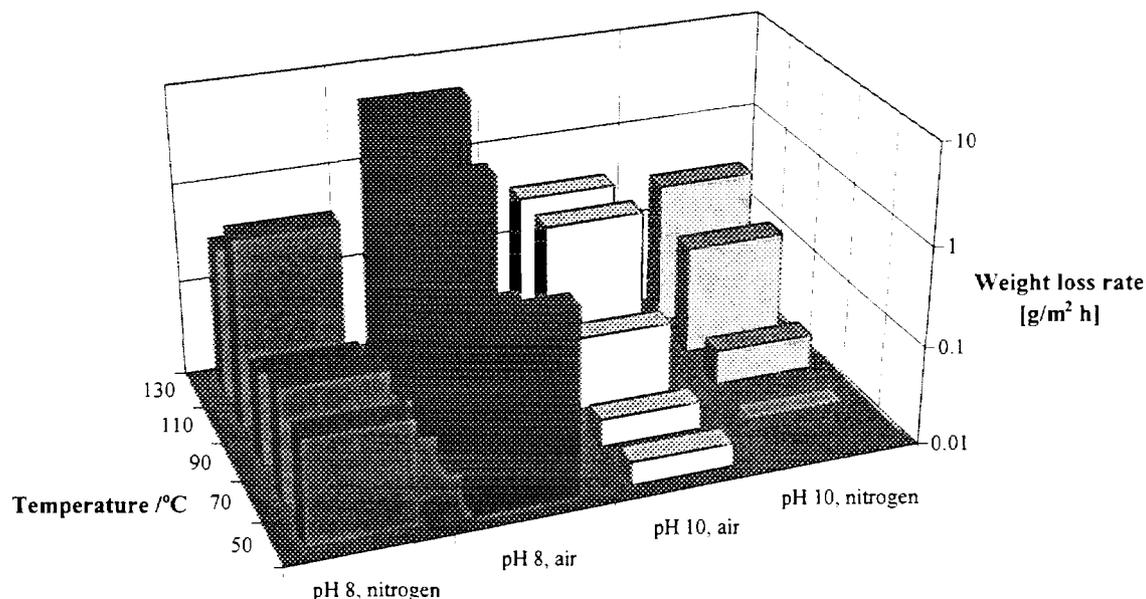
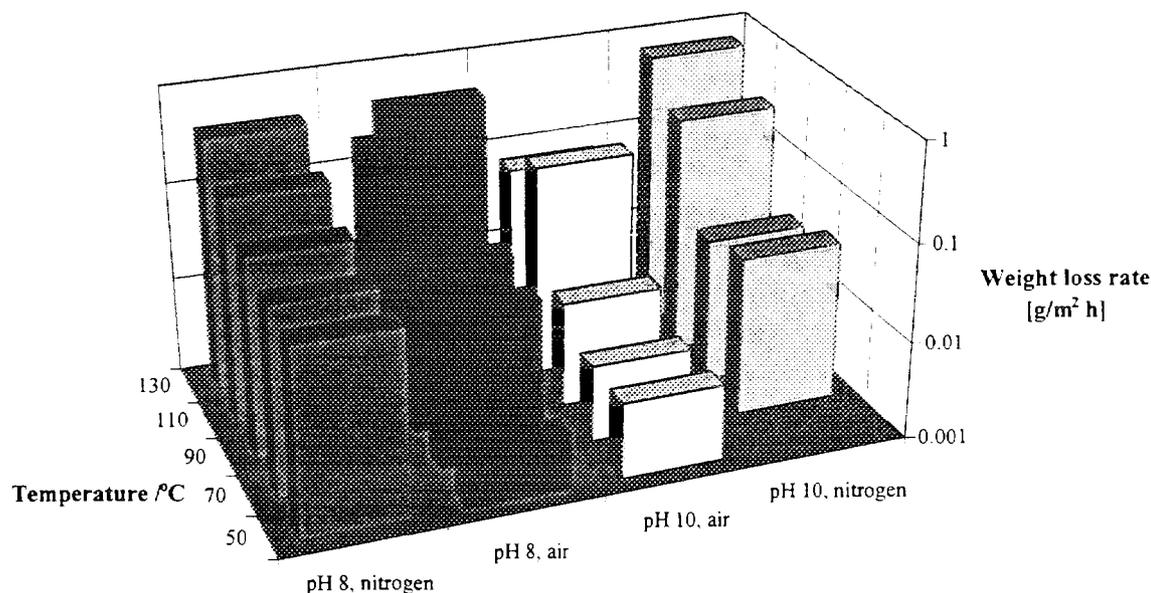


Figure 3. Corrosion rates ( $\text{g/m}^2\text{h}$ ) for aluminum as a function of pH and temperature, determined by means of the measured increase in the resistance of the corroding wires.



gas chromatography was used. They concluded that corrosion of aluminum in deionized, deaerated water was practically independent of temperature and pH and did not exceed  $0.05 \text{ mm/year}$  ( $0.015 \text{ g/m}^2\text{h}$ ). This is a very low figure compared to the recent measurements. However, this conclusion was based solely on the weight gain data. In the tests with aerated solution, in which also gas chromatography was used, the corrosion rate based on hydrogen

evolution rate was much higher than the rate based on the weight gain of the specimens. The highest hydrogen evolution rate measured in the tests was  $0.07 \text{ mol/m}^2\text{h}$  at temperature of  $150^\circ\text{C}$  and with pH of 9. This implies that aluminum was oxidized with a rate of  $1.3 \text{ g/m}^2\text{h}$  (assuming that the oxide formed is  $\text{Al}_2\text{O}_3$ ), which is quite compatible with our measurements.

For zinc, there are many results obtained using borated solutions [10,12]. The general trend that the corrosion rate for zinc is lower in basic than neutral conditions seems to be the same, as can be seen for example in the Westinghouse data as presented by van Rooyen [12]. However, the exact values differ to some extent. The scatter in the earlier results is remarkable displaying the importance of accurate measurement techniques.

Large quantities of chloride may be introduced during a severe accident, as discussed earlier. The presence of chloride is known to enhance corrosion of metals, and the results of the second test series support this also for zinc and aluminum. The tests were performed at temperature of  $50^\circ\text{C}$  with the pH varying between 3 and 11. In the tests with acidic solution, only hydrochloric acid was used for controlling pH, while in the tests with alkaline solution both hydrochloric acid and lithiumhydroxide were used. The results are presented in Table 1 and with a result from a test with pure water (pH = 7), which is included for comparison.

**Table 1. The effect of pH and chloride concentration on the weight loss rate of zinc and aluminum.**

pH	HCl-concentration mol/l	LiOH-concentration mol/l	Zn weight loss g/m <sup>2</sup> h	Al weight loss g/m <sup>2</sup> h
3	$1.0 \cdot 10^{-3}$	-	0.142	0.030
5	$1.0 \cdot 10^{-3}$	-	0.108	0.030
7	-	-	0.079	0.016
9	$5.0 \cdot 10^{-4}$	$5.6 \cdot 10^{-4}$	0.120	0.051
11	$5.0 \cdot 10^{-4}$	$7.0 \cdot 10^{-3}$	0.110	0.126

### 4.3 Results from solubility analysis

When zinc and aluminum are oxidized, both soluble species and some solid corrosion products can be formed. The nature of the solid corrosion products depends on the prevailing conditions. Generally in acidic solutions oxide compounds are produced, while high pH favors the formation of hydroxides. Also other chemicals, such as boric acid, may participate in the process leading to formation of more exotic compounds, such as metaborates.

Substantial release of soluble species to the aqueous environment at one location may lead to precipitation of solid products in other parts of the vessel, if the physical and chemical conditions (e.g. pH) vary. This is evident on the basis of Figures 5 and 6 in which the maximum concentrations of total soluble zinc and aluminum are plotted as a function of pH. The values are based on thermodynamic equilibrium calculations assuming that  $\text{Al}_2\text{O}_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{ZnO}$  and  $\text{Zn}(\text{OH})_2$  are the relevant solid compounds. The analysis was limited to these compounds, as it is anticipated they are the dominant ones especially in BWR solutions.

The corresponding maximum amounts of dissolved Al and Zn (given as number of moles) for a typical suppression pool volume of  $3500 \text{ m}^3$  are also presented in Figures 5 and 6. These values should be compared with the amounts of corrosion products formed during an accident.

Figure 5. The maximum concentration (upper curve) and the corresponding maximum number of moles (lower curve) of total soluble aluminum for a typical suppression pool volume of 3500 m<sup>3</sup> as a function of pH at 80°C.

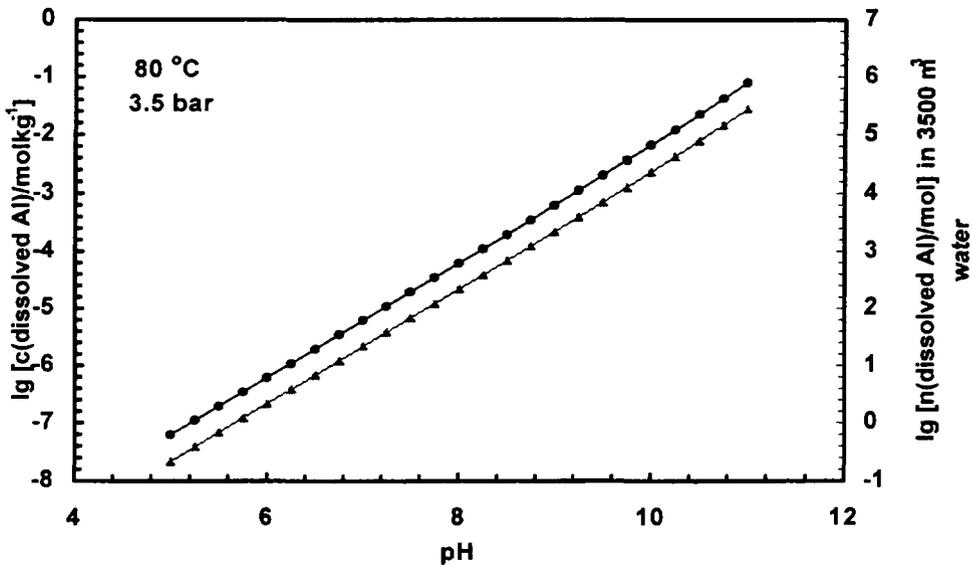
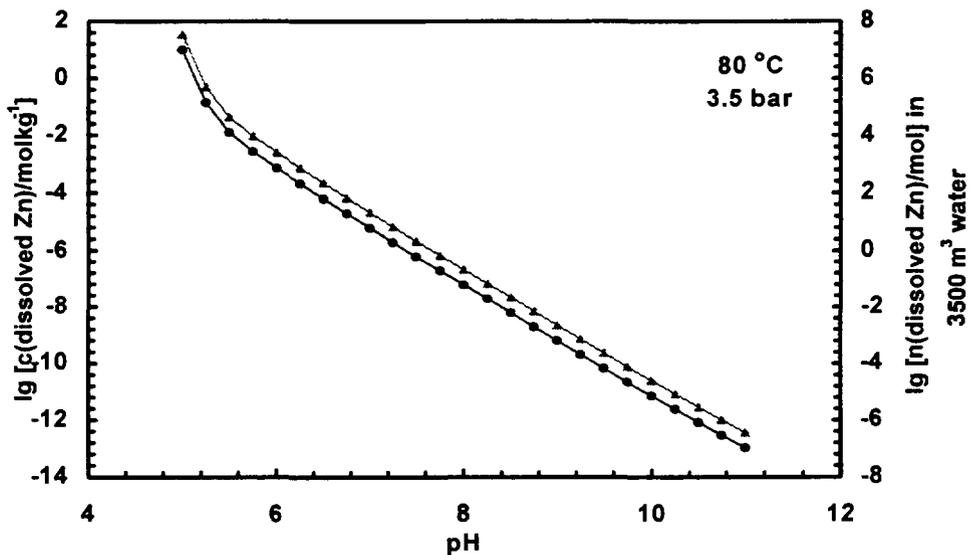


Figure 6. The maximum concentration (upper curve) and the corresponding maximum number of moles (lower curve) of total soluble zinc for a typical suppression pool volume of 3500 m<sup>3</sup> as a function of pH at 80°C.



#### 4.4 Formation of precipitates

Although complete analysis of precipitation was clearly out of the scope of the present study, some preliminary data characterizing the nature of the solid corrosion products formed in different conditions was obtained. The compositions of precipitates were characterized using

X-ray fluorescence (XRF) and X-ray diffraction (XRD) techniques. The results of the XRD diffraction analysis suggested that the precipitates formed in the tests where temperature was varied consisted mainly of zinc oxide, ZnO. However, the presence of zinc hydroxide, Zn(OH)<sub>2</sub>, cannot be excluded either. It may be present as an amorphous product, but in that case it is not detected using XRD analysis. The mean grain size of the precipitates is circa 10 µm. The scanning electron microscope (SEM) figures show that the precipitate grains have a texture resembling of cauliflower.

#### **4.5 The effects of corrosion on accident management**

The precipitates formed as a result of corrosion of zinc and aluminum may affect accident mitigation and management through various ways. Precipitation may occur on cooling surfaces, e. g. heat exchangers and reactor core channels, reducing the capacity of decay heat removal. Precipitates, together with insulation material debris generated in an accident, may clog strainers through which cooling water is sucked to emergency core cooling and spray systems. Also post-accident clean-up may be influenced, if the precipitates are carried to filters or ion-exchange units.

Although considerable attention has been paid to the effects of different materials in the suppression pool water, only the consequences of insulation material debris and sludge (consisting mainly of iron oxide) on strainer performance have been analyzed in detail [13].

However, the present results suggest that the type and amount of sludge may vary considerably, when also formation of solid oxidation products of zinc and aluminum are taken into consideration. For example, the present results imply that in a typical large break LOCA the amount of oxidized zinc may be as high as 30 g/m<sup>2</sup> after 6 hours and 55 g/m<sup>2</sup> after 24 hours in the most favorable conditions. Although there are large variations in the amount of zinc present in a containment, at least in some containments the area of galvanized steel can be high as 35 000 m<sup>2</sup> [3]. Using this value, the total amounts of zinc oxide are about 1300 kg after 6 hours and 2400 kg after 24 hours, together with 30 kg and 60 kg of hydrogen, respectively. Since much lesser amounts of sludge together with fibers have been found to cause clogging both in the experiments and in practise, this clearly underlines the importance of considering oxidation of zinc and aluminum as potential sources of precipitates.

### **5. CONCLUSIONS**

Since the suppression pool water in a BWR is not buffered during normal operation, the water pH is sensitive to the chemicals added during an accident. Should no additional buffering take place, the main factor affecting the pH may be hydrochloric acid released from the drywell cables either due to heating or irradiation.

In acidic conditions iodine may react forming elemental iodine, which could in turn react with the hydrocarbons released either from the cables or from boron carbide during an accident. Also low-molecular-weight compounds, such as methyl iodide, could be formed. These compounds are relatively volatile and they are not efficiently retained by sprays or filters usually designed for severe accident conditions. Consequently, their formation could lead to significant releases even in the case the containment remains basically intact, but pressurized.

The most efficient way of limiting formation of organic iodides is to assure that no elemental iodine is produced, i.e. to maintain high pH in the suppression pool. In the experiments conducted so far, no apparent negative effects of high pH were discovered, as much as the rate of zinc and aluminum oxidation and the nature of the solid corrosion products are concerned. However, thermodynamical calculations imply that the solubility of zinc decreases sharply as the water pH increases, while the opposite is true for aluminum.

The oxidation rates of both materials were found to be depended on temperature, redox potential and pH. Although some trends were apparent, the test results can not be considered as conclusive, in fact the scatter observed in our results, together with the previous results, indicates that large variations in the oxidation rate are possible also in real accident conditions. The same might be true also for the sludge characteristics, such as composition and size distribution. Consequently, robust solutions in prevention of any problems caused by precipitates, such as clogging of strainers, are needed.

It should be pointed out that the results presented here were obtained without using any boron in the water solution, although it is known from the previous studies that it can affect the nature of the solid corrosion products considerably. Experiments on this phenomenon are under way.

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