

# PRIMARY CIRCUIT CONTAMINATION IN NUCLEAR POWER PLANTS: CONTRIBUTION TO OCCUPATIONAL EXPOSURE

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## I. INTRODUCTION

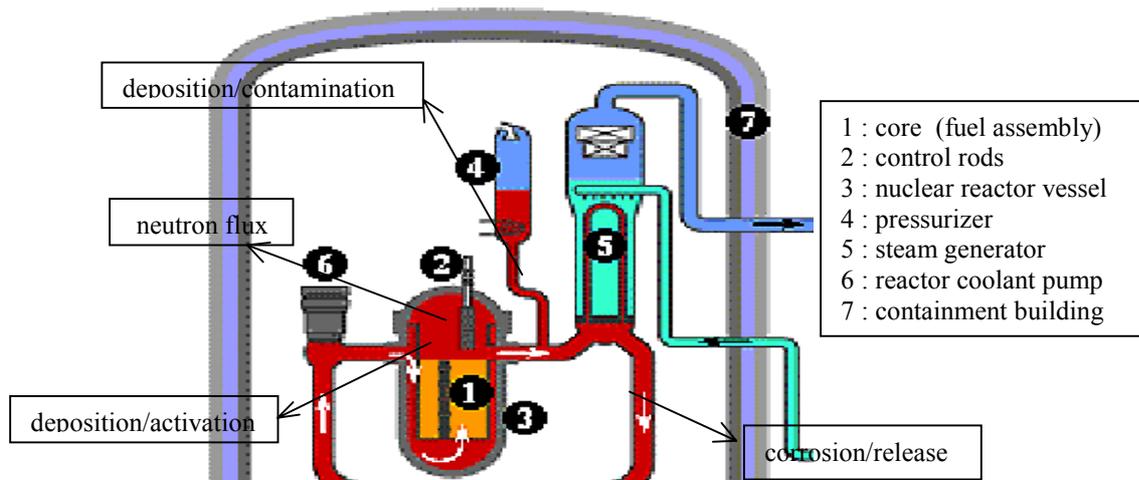
In every country since the 80's, a clear downward trend is observed concerning the occupational doses at nuclear power plants, as shows the regularly decreasing annual collective dose per operating reactor. Even if technology and work management are improving, the reduction and the control of radiation sources remain one critical point.

This paper summarizes the results of an extended study on the primary circuit contamination in nuclear power plants and its contribution to workers' exposure. The paper reviews the origin and mechanisms of radiation production and the different ways of radiation control or reduction based on physical and chemical parameters and not organisational or human factors. It underlines that chemistry control of the primary circuit is one essential component of radiation protection optimisation in nuclear power plants.

Results reported come from scientific data in open literature and cannot be generalized to all the power plants.

## II. ORIGIN OF THE RADIATION SOURCES

An operating reactor is a radiation source because of the fission reaction and of the contamination of the circuits due to corrosion as shown in figure 1. In this study only the radiation sources present after the end of the fission reaction will be described.



*Figure 1 : Radiation sources in a Pressurized Water Reactor (PWR)*

## II.1. Fission products

Fission Products (FP) come from the fission reaction which occurs in the fuel. FP are present in the primary circuit because of the impurities of uranium contained in the fuel cladding Zircaloy alloy. When a cladding defect appears, the amount of released FP rises, chiefly non volatile ones (Ba, Sr, Ce, Pr, Zr, Ru...) and actinides, which normally do not migrate out of the fuel rod. This amount depends on the length and position of the defect and on the position and the burn-up fraction of the defective fuel rod [1].

In general, uranium is in insoluble form and a very small amount is in the primary coolant. The FP are incorporated in the metallic oxides of the primary circuit surfaces as Corrosion Products do. The masses of  $\text{UO}_2$  deposited are 1 g for a clean reactor after the first cycle, 1 to 10 g for a reactor with small fuel cladding defects (below 50  $\mu\text{m}$ ) and 50 to 200 g for a reactor with broken rods.

## II.2. Activation products

Activation Products (AP) come from chemical elements activated under the neutron flux ( $^{16}\text{N}$ ,  $^3\text{H}$ ...). So, the nuclides originating from the activation of the corrosion products of the circuits are activation products too but form a special category which will be described later because of their main contribution to dose rates. The two important nuclides for radiation protection are  $^{110\text{m}}\text{Ag}$  and  $^{124}\text{Sb}$ .

Silver (Ag) comes from a leaktighness defect of control rod cladding. The  $^{109}\text{Ag}$  deposited can pass under the neutron flux and be activated in  $^{110\text{m}}\text{Ag}$  which contaminates the circuits, mainly the cold legs (steam generators).

Antimony  $^{124}\text{Sb}$  originates from a cladding defect of the start-up neutron source (Sb-Be) and the erosion of the bearings used in the main coolant pumps [2].

## II.3. Corrosion Products

Corrosion Products (CP) come from the corrosion of the structure materials in contact with the primary coolant. These are metallic elements (cobalt, iron, nickel...) directly released under an activated form or which are activated when passing under neutron flux. The main CP responsible of dose rates are  $^{60}\text{Co}$  and  $^{58}\text{Co}$ , the others are  $^{51}\text{Cr}$ ,  $^{54}\text{Mn}$ ,  $^{59}\text{Fe}$  [2,3,4].

$^{59}\text{Co}$  comes from Co-base alloys or is an impurity of the structure materials and is activated in  $^{60}\text{Co}$ . For example, stellites are an important source of  $^{59}\text{Co}$  because their release rate is higher by a factor of about 10 compared to stainless steel [5].  $^{58}\text{Co}$  is the activation product of  $^{58}\text{Ni}$ , present in Ni-base alloys or steels used for making reactor pressure vessel equipments and Steam Generators (SG) tubes.

The prediction of the Co sources varies depending on the studies as it is shown in table 1, because of the uncertainties about the transport, deposition and releasing mechanisms or cinetics of the nuclides and about their soluble or particular forms [6]. The amount of crud in the core can vary from 1 to 3 kg [7].

Table 1 : Predicted cobalt sources in PWR plants

SOURCE	Co Contribution (%)					
	A	B	C	D	E	F
<b>Co-base alloys</b>						
reactor internals	50	27				
control rod drives	6	3	9			
pump bearings	7	4	1			
valve components	30	15				
<b>Total</b>	<b>93</b>	<b>49</b>	<b>10</b>	<b>27</b>	<b>25</b>	<b>34</b>
<b>steel/ Ni-base alloys</b>						
reactor internals	1	13	6		3	28
circuits pipework			39	10		
SG	2	5	42	41	68	29
<b>Total</b>	<b>3</b>	<b>18</b>	<b>87</b>	<b>51</b>	<b>71</b>	<b>57</b>
fuel grids etc	4	31	4	22	4	10

A and B : KWU (measures)

C : EDF / PACTOLE code

D : WESTINGHOUSE / CORA code

E and F : WESTINGHOUSE/1982, 1986 (measures)

### III. MECHANISMS OF CORROSION PRODUCTS AND FORMATION OF DEPOSITS

#### III.1. Formation and circulation of corrosion products

Erosion and corrosion are the two mechanisms which cause the formation and the circulation of the CP in the circuits. Studies show that preferential releases exist for some elements compared with the base metal [6,8,9].

Soluble, colloidal or particular CP released from the surfaces are transported by the primary coolant to the core where they become activated and redistributed out of the core surfaces in the existing oxide films [10]. Soluble CP are captured by the fuel surface, eliminated by the clean-up systems or absorbed into the oxide films of the primary coolant system pipe [4]. Heaviest particles accumulate in places where the primary coolant flow rate is low or in the horizontal parts of the circuit. These deposits generate dose rate mainly in the bottom of the pressure vessel reactor and on the surface of the SG tubes. Figure 2 synthesizes the origin and the formation of deposits in a Boiling Water Reactor (BWR) [11].

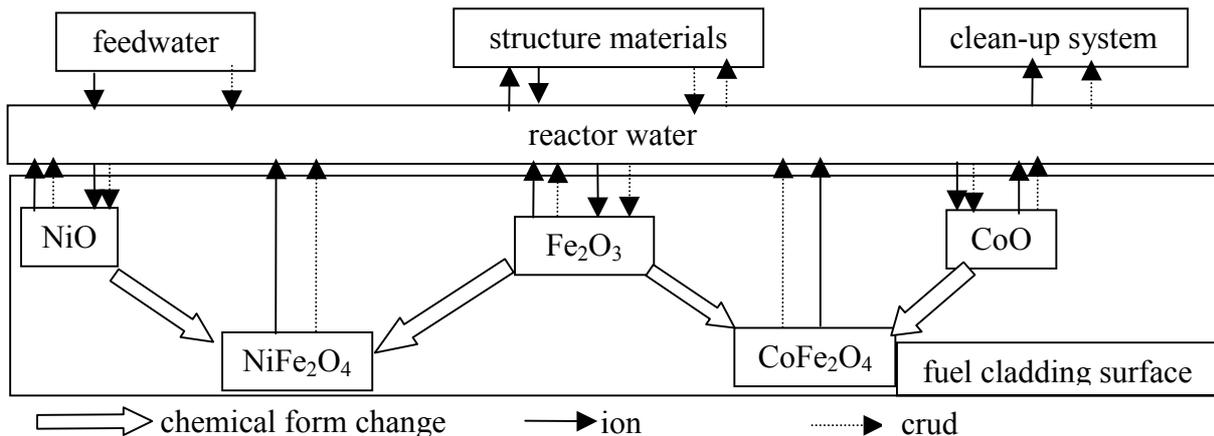


Figure 2 : Formation of deposits in a Boiling Water Reactor

Surface deposits are in general multi-layers oxides :

- the internal layer, insoluble and very thin (less than 1  $\mu\text{m}$ ), is a Cr rich spinel oxide grown on the base metal surface by solid-state processes,
- the external layer, more soluble, is a nickel ferrite combined with deposit particles, formed by metal dissolution and oxide precipitation. Fe plays the role of Co carrier.

The mechanisms of formation of the oxide layer are various : sedimentation of particles, deposition of colloids and precipitation of dissolved species. Beyond a definite thickness of the deposit, the particles flake away, this is the erosion phenomenon.

In general, oxide films are more tenacious in PWRs than in BWRs [12].

### III.2. Deposit evolution during PWR operation

The proportion of CP and their physico-chemical form (particular, soluble or submicronic) vary during operation cycles. In France, for PWRs, <sup>58</sup>Co dominates in the first cycles of operation whereas <sup>60</sup>Co accumulates because of its longer period [13,14].

Cold shutdown is a special step in the operation of a power plant because the volumetric activity and the amount of particles of CP released in the coolant increase significantly when the temperature decreases. The cold shutdown procedure must :

- minimize the release or the dissolution of CP under flux to avoid primary circuit contamination,
- quickly reduce the primary water activity and the time between reactor shutdown and opening of the vessel head,
- facilitate the fuel handling operations by maintaining water purity and reducing surface dose rates of the reactor well [15].

Cold shutdown comprises three phases [15,16] :

1. power reduction during which rapid variations in the volumetric activity occur because of the release of  $^{58}\text{Co}$  rich particles originating from in-core deposits, due to temperature changes and mechanical effects during the control rod movements. These particles are filtered or redeposit quickly. The released activity during this step is small compared with the total activity released during shutdown.
2. cooling and borification of primary water induce an increase of the volumetric activity of the Co isotopes which are mainly in soluble form and of the Ni concentration. Between 280 and 170°C, activity transfers are low and variations of out-of-core deposited activity are nil. Below 150°C, in-core deposits are dissolving. In fact, the dose rate variations are due to variations in volumetric activity in the primary and other circuits and not due to deposited activity.
3. oxygenation occurs when the temperature varies between 50 and 90°C and induces a sudden increase of the Ni concentration and of the volumetric activity of the Co-radionuclides, and a decrease of the Fe quantity. A part of pure Ni deposits that had remained in neutron flux dissolve whereas out-of-core deposited activity does not decrease. The main part of the released activity during shutdown occurs during oxygenation and comes from in-core deposits. Oxygenation promotes  $^{109}\text{Ag}$  and  $^{110\text{m}}\text{Ag}$  release too. If the oxygenation temperature is too high, an important  $^{58}\text{Co}$  recontamination and an elemental Ni and Co deposition can happen on the primary circuit surfaces.

It is important to note that the Ni-rich oxide deposits are very sensitive to the conditions of shutdown unlike mixed ferrites. Simple correlations between released activities during shutdown and normal operation do not exist as shown in table 2 according to a EDF's study [17]. Eventually, the movements of hot spots follow those of water and can impact greatly on financial and dosimetric aspects of the shutdown operations.

*Table 2 : Measured activities in the primary circuit in normal operation and during oxygenation*

	Co58	Co60	Sb124	Ag110m
Normal (MBq/t)	10-100	1-10		
Shutdown (GBq/t)	100	3	10	2

#### **IV. REDUCTION OF RADIATION SOURCES**

Several parameters influence the dose rates measured in power plants : materials, coolant chemistry, temperatures and circuit flow rates, composition and structure of the oxide layers and CP carried by the coolant, plant capacity and age, wear of equipments, regulation systems, thermal and surface treatments of structural metals... [5, 12,18,19].

Improvement in operational management, primary coolant chemistry optimisation and decontamination processes have contributed to the reduction of occupational radiation exposure in power plants [2,20]. Today, new ways would make possible a reduction of the dose rates [11,21]:

1. controlling the source : minimize cobalt impurities in structure materials, eliminate cobalt from in-core materials and substitute cobalt-base alloys in the valves by developing low-cobalt or cobalt-free alloys,
2. controlling transport and activation : optimize water chemistry, control pH, inject some ppb of zinc in BWRs,
3. controlling out-of-core deposition : precondition the primary system surfaces to reduce CP deposition rate by electrochemical or mechanical polishing and chemical preoxidation.

#### IV.1. Use of low-cobalt alloys

Replacement of cobalt-base alloys to reduce dose rates in the primary circuits is cost effective. For example, in Germany, change in material concept (use of corrosion resistant and low-cobalt alloys) contributed to reduce the occupational radiation exposures between 0,1 and 0,4 man.Sv per year at the new Siemens designed PWRs [2].

#### IV.2. Electropolishing and structure material treatment

Surface electropolishing reduces microroughness and deposition rate; that is an effective method to decrease dose rates, mainly for Steam Generators. At the opposite, rough or damaged surfaces have higher activity uptake and corrosion release rates [22]. The pre-oxidized materials have less deposits too, because a passive protective film of oxide is formed at the surface before their exposition to the coolant [21]. Decontamination influences the deposition rate on the surfaces too, it can be greater after decontamination [12].

#### IV.3. Primary coolant chemistry optimisation

Controlling the primary coolant chemistry is obtained by filtration, pH, redox potential... in order to reduce the transport and the solubility of CP, in particular  $^{60}\text{Co}$  [12,21]. Some ways are described below.

- pH greatly influences the solubility of the elementary constituents of base materials and oxide layers. Practically, pH is controlled by lithium and boric acid concentrations. Today, in most cases the [lithium]/[boric acid] ratio generates a 6,9-7 pH approximately at 300°C, which corresponds to the minimum of magnetite solubility, the major PWR oxide [19]. Nevertheless, the use of higher pH about 7,2 is studied because it would reduce the corrosion of the structure materials of the primary circuits, the CP release and transport. However a too high lithium concentration may increase fuel cladding corrosion [17,23,24].
- Redox potential influences more BWRs than PWRs. Generally, entrance of oxygen in the circuits is detrimental for PWR but few studies have been made about this complex problem which still remains under investigation [4,12,25].
- Zinc injection reduces corrosion of stainless steel, in-core cobalt-base alloys and  $^{60}\text{Co}$  concentration in reactor water and its capture on pipe surfaces [20,21,26]. Some American studies demonstrated a 25 to 30% dose rate reduction at the steam generators channel heads

after one zinc injection cycle [20]. This is a cost effective and easy to implement technique for radiation field control and has no adverse effects on BWR plant circuits and fuel materials.

- Control of Ni/Fe ratio in feedwater and iron injection have been used since the 80's in Japanese BWRs to decrease cobalt concentration in reactor water. Because of circuits contamination problems with this process in recent Japanese plants, a new conditioning, the "Ultra-Low-Crud/High Ni" (ULC-HN) was developed to keep as low as possible the amount of crud deposit on the fuel cladding surfaces and the deposition rate of nuclides on out-of-core surfaces as well. To make it possible, they reduce the iron concentration in feedwater and they keep relatively high nickel concentration in water reactor. The interaction mechanism between nickel and cobalt is similar to that between zinc and cobalt. With this conditioning, the oxides on fuel cladding surface are more soluble than the ferrites usually found on the pipe or fuel cladding surfaces and they can be removed by reactor water clean-up systems. So, they do not represent a significant source of  $^{58}\text{Co}$  and  $^{60}\text{Co}$  [11,25,27].

#### IV.4. Conclusion

It is important to note that great amounts of deposits cannot be eliminated by one punctual change in the chemical conditioning, and that the contamination is minimized when the chemical parameters are stable during operation [18]. First, it is essential to reduce the mass of iron-rich cruds and the generation of cobalt. Next, it will be possible to control the iron-rich crud concentration by controlling the Ni/Fe ratio. Eventually, the use of pre-oxidized materials will be effective [11].

#### **V. OCCUPATIONAL RADIATION EXPOSURE STAKES**

The collective occupational radiation exposures result from three factors : the radiation source, the shielding design and the time of operation in the radiation field.

According to C.J. WOOD, in American nuclear power plants, the average collective dose decreased from 12,5 to 4,5 man.Sv per reactor and year for BWRs and from 6 to 3 man.Sv per reactor and year for PWRs between 1980 et 1990 [28]. In Germany, the average collective dose at Siemens designed PWRs were approximately 5,2, 3 and 2 man.Sv per reactor and year respectively in 1980, 1985 and 1992 [2]. In recent Konvoi designed plants, the average collective dose is 0,2 man.Sv per reactor and year. In France, according to EDF, the average collective dose has been decreasing of 60% since 1991 and 5% between 1998 and 1999. Nowadays, the average values for 900 and 1300 MWe plants are respectively 1,42 and 0,73 man.Sv per reactor and year [29].

It appears very difficult to associate occupational radiation exposure and dose rate because very few data exist. According to a German study on Siemens designed PWRs, about 80% of the  $\gamma$  radiation is produced by  $^{60}\text{Co}$ , 20% by  $^{58}\text{Co}$  and 10% by  $^{124}\text{Sb}$  [2]. Nevertheless, in some recent plants with new materials concept,  $^{60}\text{Co}$  activity concentration contributes only for 50% to the measured dose rates on the surfaces of the primary circuit and  $^{58}\text{Co}$  activity concentration for 40%.  $^{124}\text{Sb}$  remains a significant source of dose rates in France because it is still employed in some equipments.

The Fission Products do not represent an important source of primary circuit surfaces contamination and do not generate significant dose rates, less than 5% even when there is a severe defect in fuel cladding [30].

Finally, 5% of the collective occupational radiation exposure is due to neutrons. According to EDF, it represents less than 0,3 man.Sv per year for French nuclear power plants [29].

In France, about 80% of the collective dose at EDF nuclear power plants is related to plant shutdowns. That represents about half of collective dose registered for all the sectors of activities in France. The contribution of hotspots to shutdown dosimetry can vary from 20 to 30% [24,31].

## **VI. CONCLUSION**

This bibliographical study shows that the origin and the formation of radioactive deposits are very complex and vary from one plant to another because they strongly depend on the operating conditions as coolant chemistry, structural materials... The major contribution of Corrosion Products and their origin are well established today. Several researches are made to change some parameters in order to reduce the sources of contamination and the formation of deposits which concentrate Corrosion Products. Zinc injection, replacement of cobalt-base alloys, reduction of cobalt impurities in stainless steel, coolant chemistry optimisation and surface treatments for structural materials are the main possibilities.

Most of the studies presented herein consider the punctual influence of different parameters on deposit formation. In these studies, it's possible to quantify the effect by the estimated mass or activity of the deposit. Other studies done in operating plants give a global and actual point of view of the phenomena, through dose rates measurements near contaminated surfaces. On the other hand, the assessment of the occupational radiation exposures is hardly tackled or remains imprecise because it integrates numerous parameters which sometimes cannot be quantified. So, it is very difficult to relate directly the change of a parameter concerning chemical conditioning or materials to the occupational radiation exposures of workers. Finally, changing some coolant chemistry parameters in order to reduce occupational radiation exposures during maintenance is much more expensive than improving operating procedures. Today, considering the great efforts already made on equipments, shielding and work management, coolant chemistry optimisation could represent a promising and effective way for the future to reduce the occupational radiation exposure [4].

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