



HAL
open science

Insights into the formation mechanism of hard sludge on the secondary side of PWR steam generators

Kevin Beal, Lisa Million-Picallion, Sophie Delaunay, Gilles Berger, Grégory Lefèvre

► To cite this version:

Kevin Beal, Lisa Million-Picallion, Sophie Delaunay, Gilles Berger, Grégory Lefèvre. Insights into the formation mechanism of hard sludge on the secondary side of PWR steam generators. Nuclear Materials and Energy, 2022, 31, pp.101197. 10.1016/j.nme.2022.101197 . hal-03807951

HAL Id: hal-03807951

<https://hal.science/hal-03807951>

Submitted on 10 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Insights into the formation mechanism of hard sludge on the secondary side of PWR steam**
2 **generators**

3

4 K. Beal^{1,2}, L. Million-Picallion³, S. Delaunay¹, G. Berger³, G. Lefèvre²

5

6 ¹ EDF, R&D/Chemistry and Corrosion Group, Av. des Renardieres, 77818 Moret-sur-Loing, France

7 ² PSL Research University, Chimie ParisTech - CNRS, 75005, Paris, France

8 ³ IRAP, CNRS- Université Paul Sabatier, 14 Av. Edouard Belin, 31400 Toulouse, France

9

10

11 **Abstract**

12 In the secondary circuit of nuclear Pressurized Water Reactors, corrosion products and impurities
13 lead to the formation of undesirable hard deposits, called hard sludge, on the tube sheet of steam
14 generators. These deposits are mainly composed of iron (magnetite), alumina and silica. The
15 formation of hard sludge piles is investigated by reproducing the reaction of precursor oxides in the
16 conditions of the steam generator (275°C, 58 bar). Mixtures of magnetite, γ -alumina and amorphous
17 silica in binary or ternary systems in an alkaline ethanolamine-ammonia solution at pH_{25°C} = 9.6 are
18 studied. Carbon steel was tested as an alternative source of iron.

19 The analysis of the evolution of the suspensions, completed by the industrial feedback, allows to
20 explain the process of hard sludge formation in the steam generators. The following sequence is
21 proposed: sedimentation of magnetite / confinement of the interstitial fluid / concentration of
22 aqueous species such as aqueous silica and alumina / sorption of Al on magnetite and/or growth of
23 boehmite / reaction with aqueous silica to form kaolinite as a resistant cement. Once formed, the
24 kaolinite cement tends to densify over time while magnetite is passive. The absence of Fe-

25 phyllosilicates predicted by thermodynamics is explained by the low solubility of magnetite making
26 unfavorable the precipitation of Fe-silicate.

27 By contrast, metallic iron is not stable at contact with water and the continual production of
28 divalent iron, whose solubility is much higher than that of magnetite, allows to overpass a threshold
29 concentration what makes possible the precipitation of a berthierine layer at the surface of corroded
30 steel. This layer constitutes the nucleation site for the further precipitation of other aluminosilicates.

31

32

33 Keywords: alumino-silicates ; thermodynamic modelling ; phase characterization ; hydrothermal
34 reactions

35

36

37 **1. Introduction**

38 The hydrothermal crystallization of silicates phases in the Si-Al-Fe system may lead to industrial
39 constraints that can be encountered in the nuclear industry in at least two contexts: the geological
40 repository for nuclear wastes and the formation of hard sludges in the steam generator of the
41 Pressurized Water Reactors (PWR) nuclear plants. In the first situation, the chemical reactions
42 between the Fe-canister and the surrounding clays have been extensively studied in laboratory [1] [2]
43 [3] [4] [5] [6] [7] and pilot experiments [8]. By contrast, the formation of deposits with this
44 composition in the steam generators of PWR plants, called hard sludges, is a newer and less studied
45 issue that can affect the reactor performance.

46 In the secondary circuit of nuclear Pressurized Water Reactors, corrosion products and impurities
47 lead to the formation of hard deposits on the tube sheet of steam generators (SG). These deposits
48 could lead to SG tubes denting, or a local increase of temperature, which could then promote stress
49 corrosion cracking of SG tubes [9]. Although magnetite is the main compound, high impurities
50 concentrations, in particular aluminum and silicon oxides, are found in hard sludge compositions [10]
51 [11]. Mechanisms that lead to the formation and consolidation of hard sludge have not been
52 identified [12]. Analysis of sludge pile deposits from plants suggests that the impurities may have a
53 significant role in their formation [13]. Some studies [14] [15] have also reported that minor
54 impurities, such as calcium and zinc, can be involved in deposits consolidation mechanisms by
55 forming new phases such as willemite (Zn_2SiO_4) or calcium sulfate.

56 Despite their complex structure and composition, a simplified model of hard sludge may be
57 proposed: an aluminosilicate matrix containing the magnetite particles. This simplified model
58 constituted the frame of our study. A previous experimental study [16] [17] focused on the first stage
59 of hard sludge formation: the sorption of aqueous aluminum or boehmite precipitation at the surface
60 of magnetite particles acting as nucleation sites for the further growth of silicate. The aim of this
61 experimental study focuses on the second stage of the process: the conversion of precursor

62 (magnetite (Fe_3O_4), alumina ($\gamma\text{-Al}_2\text{O}_3$), silica (SiO_2)) into consolidated hard sludge, and to better
63 understand the formation mechanisms and the role of the different parameters (chemical species
64 and time).

65 We lead to react at 275°C assemblages of alumina, silica and magnetite, as well as binary systems,
66 in an alkaline solution modeling the secondary circuit fluid. The mineral transformation was
67 characterized after one to few weeks of reaction by appropriate technics and compared to
68 thermodynamic predictions. We also tested carbon steel as an alternative source of iron.

69

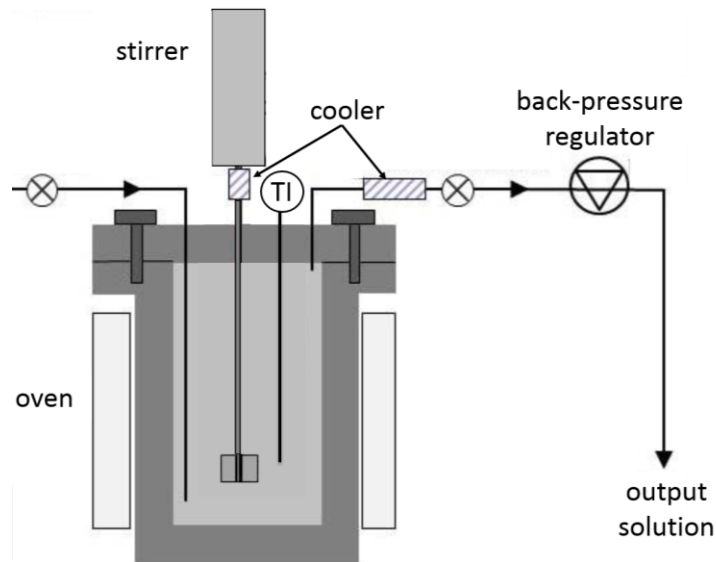
70 **2. Materials and methods**

71 In steam generators, sedimentation on the top of the tube sheet creates a confined media where
72 the fluid circulation is minimal and where impurities may reach higher concentrations leading to the
73 formation of new mineral phases. We experimented this confined media by using a hydrothermal
74 reactor used in a static closed system. In addition to magnetite, the impurities were introduced in the
75 system in the form of oxides powder, i.e. γ -alumina ($\gamma\text{-Al}_2\text{O}_3$) for aluminium and amorphous silica
76 (SiO_2) for silicon.

77 *2.1. Experimental facility*

78 The experimental device (Figure 1) is based on a 450 mL commercial reactor (Parr Instrument©)
79 made of pure titanium (grade 4) and used in a static mode, where the system remains closed during
80 tests, without flow of the solution. The internal volume of the vessel is stirred by an impeller (around
81 200 rpm), driven by an external magnetic driver, and the temperature is controlled with an immersed
82 thermocouple. This device is connected to a back-pressure regulator.

83



84

85

Figure 1. Scheme of the experimental design

86

87 2.2. Test conditions

88 The static experiments presented here were conducted at 275°C under vapor pressure, i.e. 58 bar.

89 PWR secondary circuit chemistry is reproduced using an alkaline solution at $\text{pH}(25^\circ\text{C}) = 9.6$ containing

90 3 ppm concentration of ethanolamine and 1 ppm of ammonia. 1 ppm of N_2H_4 was added to remove

91 the remaining trace of oxygen but it decomposed quickly during the heating.

92 Several parameters were continuously monitored, as pressure, temperature and stirring rate. A

93 solution sample was regularly withdrawn (around 6 samples during an experiment) to measure the

94 pH and the concentration of amines and mineral species. The followed protocol was (1) stopping the

95 stirring to allow particles to settle, (2) withdrawing the cooled solution, (3) filtering it (filter 0.2 μm).

96 Proportions of oxides were calculated according to hard deposits compositions removed from

97 steam generators of several countries [10]. Tests were first performed with the three simultaneous

98 oxide additions at several different times. Table 1 summarizes all these tests conditions.

99

100

101

102

103 *Table 1. Composition of the reacted the ternary oxide mixture*

Element	Solid	Concentration of solids (g/L)	%w of solids	Concentration in elements (mM)
Fe	Magnetite	10	62	43
Al	γ -alumina	3.9	24	38
Si	Silica	2.2	14	37

104

105 In addition to these reference experiments, binary systems using alumina + magnetite, alumina +
 106 silica or silica + magnetite were experimented. We also conducted runs using carbon steel (metallic
 107 iron) as the source of iron instead of magnetite. Table 2 summarizes this second set of experiments.

108

Table 2. Experimental conditions

Solids	Time at 275°C
Magnetite + silica + alumina	7 days
	18 days
	30 days
	180 days
Magnetite + alumina	30 days
Alumina + silica	
Magnetite + silica	
Carbon steel + alumina + silica	

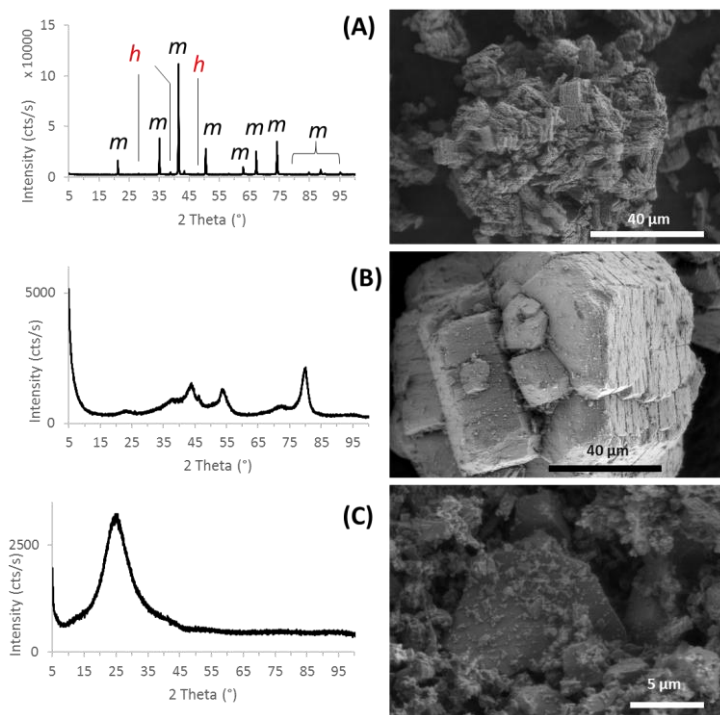
109

110 *2.3. Chemicals*

111 γ -alumina is provided by Merck© under the reference 01095 (purity > 99.5%). The magnetite and
 112 amorphous silica samples are high purity chemicals commercialized by Alfa Aesar© (ref. 12962 and

113 89709, respectively). X-Ray diffractograms and microscopic observations of the starting reactants
 114 are shown in Figure 2. The magnetite sample shows few % of hematite impurity.

115



116

117 *Figure 2: Diffraction patterns (left) and microscopic observations (right) of the starting reactants: (A)*
 118 *magnetite (diffraction peaks of magnetite and hematite are indicated by m and h, respectively), (B)*
 119 *alumina, (C) silica.*

120 The composition of the carbon steel used in the second set of experiments is reported in Table 3.

121

122 *Table 3. Minor elements content in 18MNDS steel*

Element	Al	C	Co	Cr	Mn			
%w	0.024	0.199	0.01	0.19	1.56			
	Mo	N	Nb	Ni	P	S	Si	Ti
	0.53	0.0036	0.01	0.64	0.002	0.001	0.22	0.01

123

124 2.4. Characterizations

125 The morphology of the film surface was imaged with a high-resolution Sigma Zeiss scanning
126 electron microscope (SEM) at an acceleration voltage between 5 and 10 kV, and additional
127 characterizations of the film surface were conducted using secondary electron imaging and energy-
128 dispersive X-ray spectrometry (EDX). The crystallographic structure of the film was characterized by
129 X-ray diffraction (XRD) using a Rigaku Geigerflex with a Co anode, or a Bruker D8 Discover with a Cu
130 anode. μ Raman spectroscopy has been performed using a Renishaw InVia Reflex with a 532 nm laser.

131 One sample has been analyzed using a transmission electron microscope (MET) OSIRIS 200kV
132 after its preparation using a focused electron beam in Scanning Transmission Electron Microscopy
133 High-Angle Annular Dark-Field (STEM HAADF) mode.

134 Solutions have been analyzed with an Inductive Coupled Plasma – Atomic Emission Spectroscopy
135 (ICP-AES) ThermoFischer iCAP 6500.

136

137 2.5. Numerical modeling

138 Speciation calculations of the solid-solution systems investigated have been performed using the
139 software CHESS [18], a geochemical simulator developed to simulate the water-mineral interactions.
140 The associated database included in the software package was completed with data coming from
141 MultEQ database, an improved database developed by Electric Power Research Institute to address
142 high temperature chemistry, especially in cooling circuits of PWR.

143

144

145 3. Results

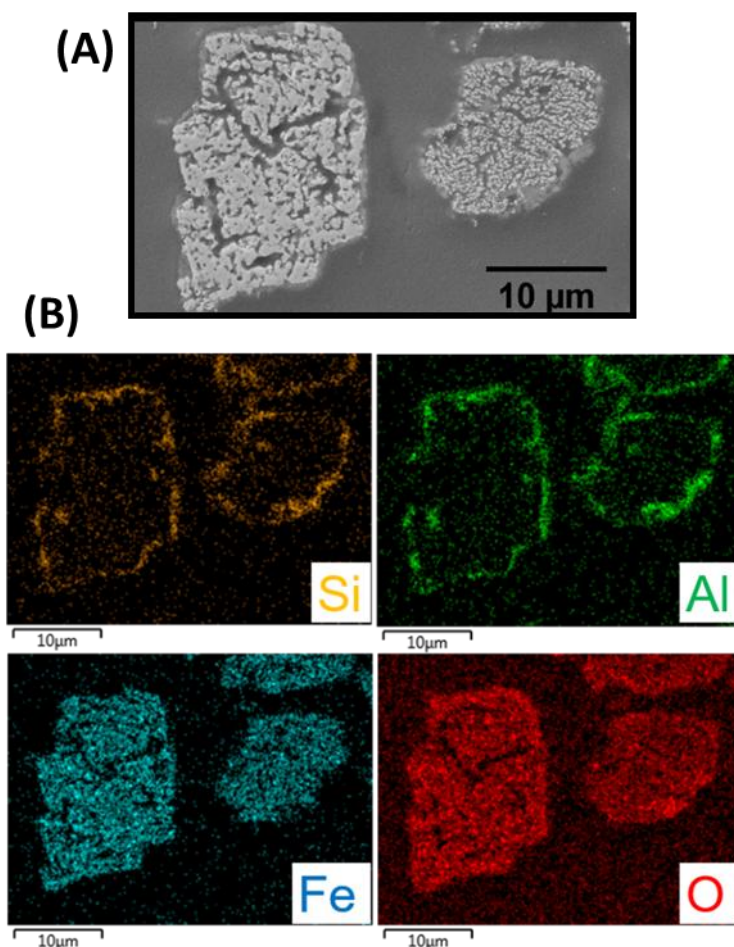
146 Sampling aliquots of solution during the course of the experiments allowed to monitor changes in
147 the fluid chemistry with time. The aqueous concentration of Si and Al increased and remained in the
148 100-200 ppm range for silica and 2-4 ppm range for alumina from ca. 180h. The pH decreased of 1

149 unit, in agreement with calculations indicating that it is due to the formation of negatively charged
150 silica species. The main effort concerns the characterization of the mineral by-products. We first
151 present the Si-Fe-Al system that is representative to the industrial environment. In a second stage,
152 we will explore binary subsystems and an alternative source of iron in order to better discuss the
153 results of the reference system.

154

155 3.1. Ternary system (magnetite+alumina+silica)

156 After a 7-day ageing period, the mixture of magnetite-alumina-silica has been observed by SEM-
157 EDX (Fig. 3). The sample consists of particles of about 10 μ m sized, with the same microporosity as
158 the magnetite added in the reactor. The EDX analysis confirms the composition (only Fe and O). On
159 the other hand, it can be observed that both aluminum and silica are accumulated on the edges of
160 the magnetite particles.

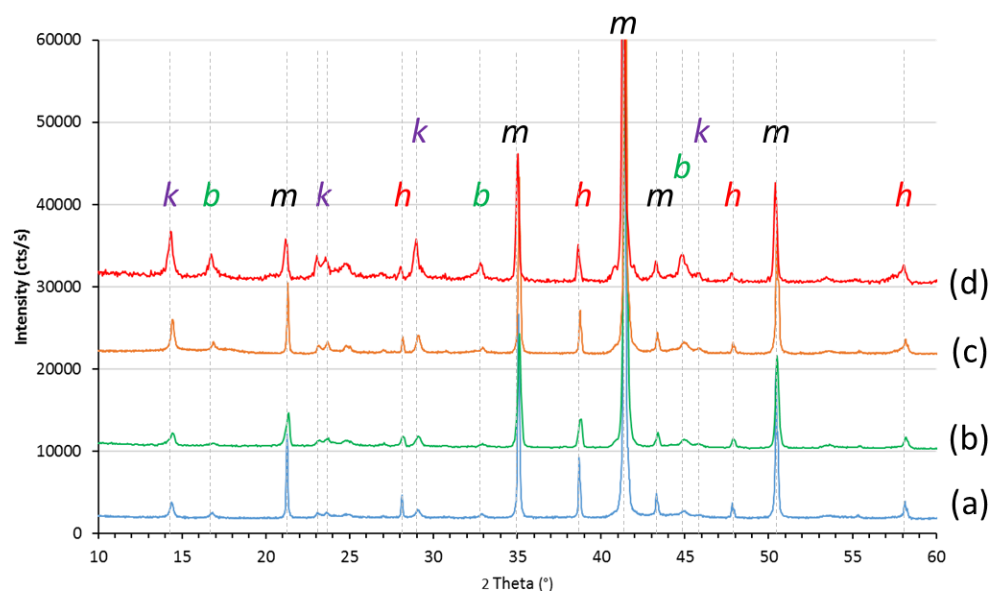


161

162 *Figure 3. Pictures of sample cross-section after a 7-day ageing period: (A) secondary electron SEM,*
163 *picture and (B) EDX mapping for the four elements indicated.*

164 The diffractogram of this sample (Fig. 4) is dominated by the peaks of magnetite (with some
165 impurities of hematite whose content seems constant), with the presence of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$)
166 and boehmite ($\gamma\text{-AlO}(\text{OH})$). This latter phase is expected, due to the hydration of γ -alumina in
167 hydrothermal conditions [19], while kaolinite comes from the reaction between silica and γ -alumina.
168 The molar ratio of Al/Si in the system is around 1, as in the formula of kaolinite, so boehmite is not
169 formed due to an excess of aluminum.

170



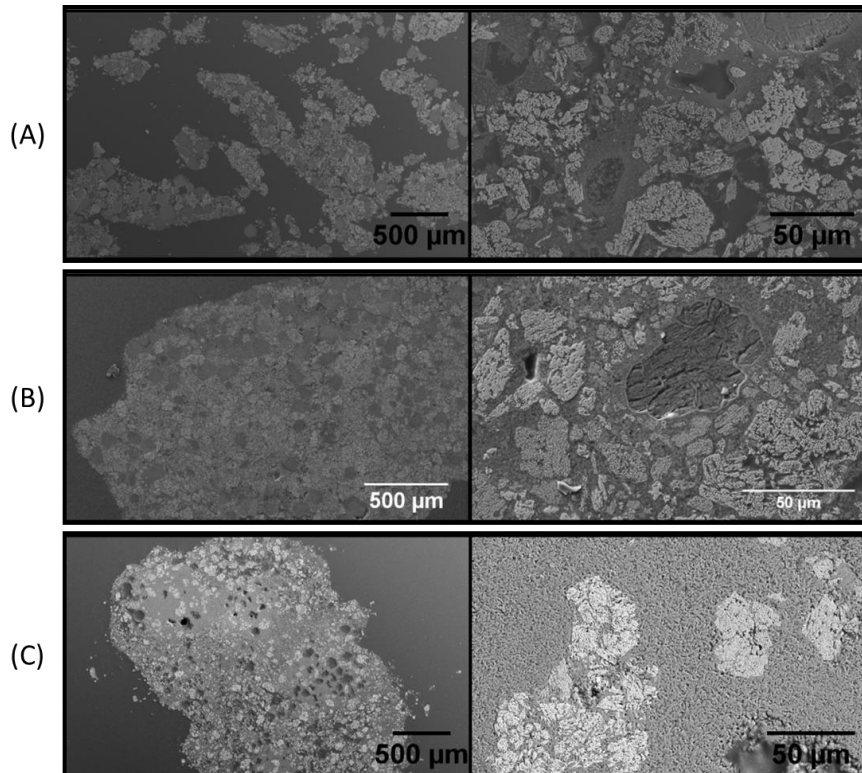
171

172 *Figure 4. XRD analysis of samples as a function of ageing, after (a) 7 days, (b) 18 days, (c) 30 days*
173 *and (d) 180 days. The peaks identified for magnetite (m), hematite (h), kaolinite (k) and boehmite (b)*
174 *are detailed.*

175

176 The pictures in Fig. 5 show samples after different ageing periods. While the SEM picture after a
177 7-day ageing period showed no evolution compared to pristine magnetite, the pictures show a
178 growth of the size of the particles, with the formation of millimetric agglomerates.

179



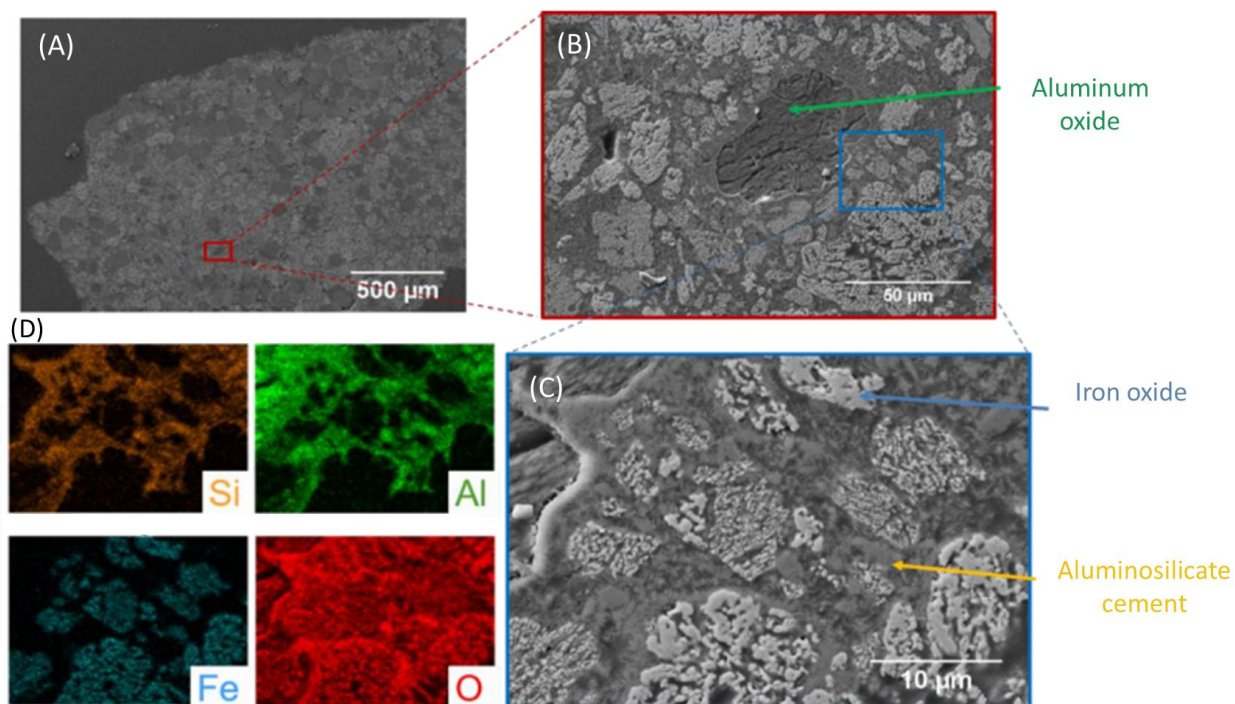
180

181 *Figure 5. SEM picture of samples cross-sections after different ageing periods: (A) 18 days, (B) 30 days*
182 *and (C) 180 days.*

183

184 In the diffractograms (Fig. 4), the peaks corresponding to kaolinite and boehmite increase, to
185 reach a maximum at 180 days. A detailed analysis for 30-day ageing is presented in Figure 6. EDX
186 maps in Fig. 6C shows several phases: magnetite particles remain free of Si and Al, and looks like the
187 pristine solid, and some particles of γ -alumina are visible. However, no particle of silica has been
188 identified (which would correspond to a zone in EDX map free of Al and Fe), but on the contrary, Si is
189 systematically associated with Al and is present around each particle of magnetite or γ -alumina. This

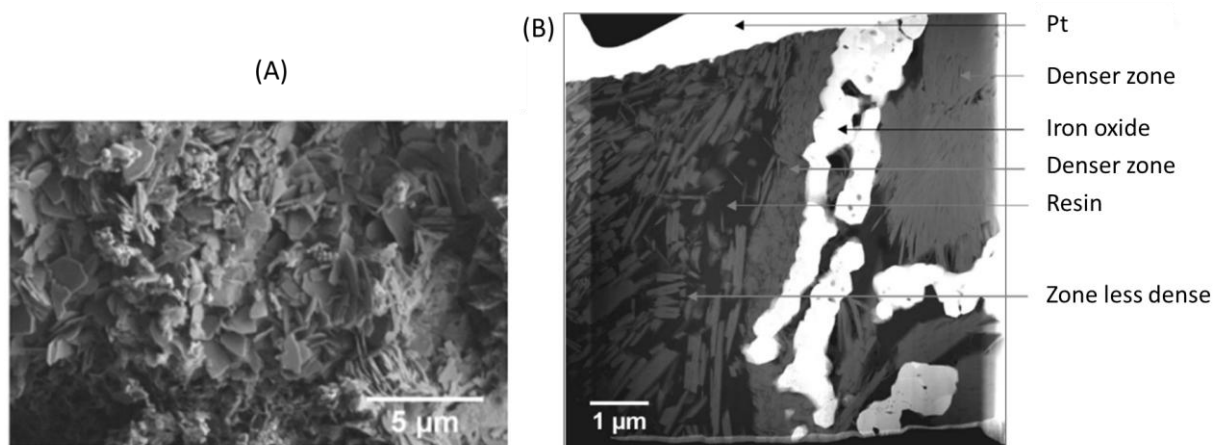
190 picture shows undoubtedly that an aluminosilicate plays the role of cement to consolidate the
191 sample initially consisting in dispersed particles in suspension.



192
193 *Figure 6. Cross-section of sample after 30-day ageing: (A) to (C) SEM with increasing magnification,*
194 *and (D) EDX map of (C) picture.*

195
196 To go further in the understanding of the structure of the sample, its surface has been observed
197 by SEM (Fig. 6). It was found to be covered by layers, whose geometry is typical of clays. The MET
198 STEM HAADF (Fig. 7) shows the cross section of these layers, stacked in a non-compact way. On the
199 contrary, in the vicinity of the magnetite particles, a dense zone is observed where the layers look
200 oriented parallel to the surface of the particles, and seem to have merged. The cement observed in
201 previous figures is present in two distinct forms: the denser zone would result from a growth of the
202 clay at the surface of the magnetite, while the non-compact zone would result from the
203 agglomeration of precipitated layers, due to settling or electrostatic interactions.

204



205

206 *Figure 7. Sample after 30-day ageing: (A) SEM and (B) STEM HAADF*

207

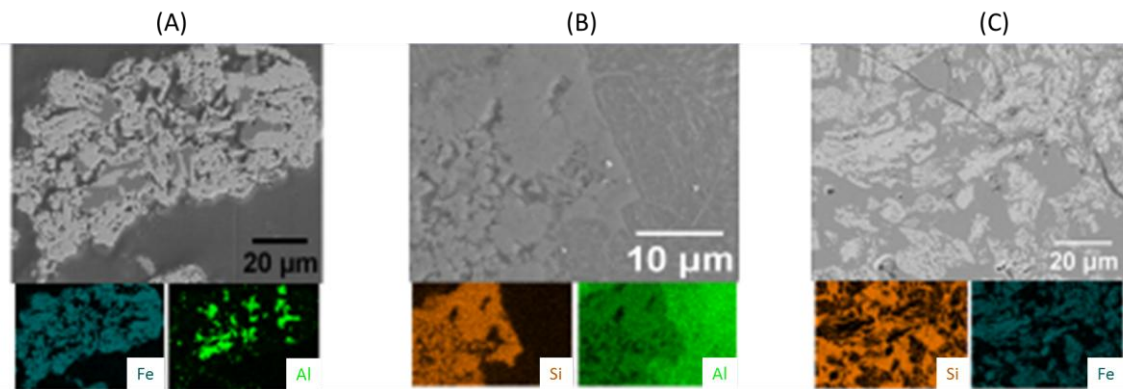
208 3.2. Binary systems

209 The previous experiments have shown that the reason of the consolidation is the formation of a
 210 cement consisting in kaolinite. Binary systems have been experimented to evaluate the specific role
 211 of Al and Si. It could also bring interesting results on the consolidation in the case of a Si/Al ratio far
 212 from 1, which is possible in steam generators.

213 In Figure 8 we reported the SEM-EDX observations relative to the three binary systems. In
 214 absence of magnetite, the sample consists in alumina particles (on the right of the Fig. 6B) mixed
 215 with kaolinite (on the left). XRD analysis (not shown) reveals only boehmite and kaolinite. It can be
 216 concluded that magnetite is not needed to trigger the formation of kaolinite, what is consistent with
 217 the kaolinite layers found far from its surface (Fig. 6). In the magnetite-alumina system, boehmite
 218 and diasporite have been identified by XRD. The SEM-EDX analysis shows the precipitation of
 219 aluminium hydroxide (identified as diasporite by μ Raman) in the porosity of magnetite particles with a
 220 low amount of aluminium at the external surface of magnetite. Moreover, no consolidation has been
 221 observed, which indicates that the aluminium hydroxide is not able to play the role of cement
 222 between magnetite particles. However, its high affinity towards this iron oxide is demonstrated, and
 223 this surface accumulation of aluminium would allow the growth of kaolinite on its surface. In the

224 magnetite-silica system, some consolidation is locally observed, and the SEM-EDX show opposite
225 maps for Si and Fe. The magnetite particles are embedded in a silica gel coming from the dissolution
226 of silica particles. No crystalline phase except iron oxides is detected in diffractogram.

227



228

229 *Figure 8. SEM pictures and EDX map of binary systems: (A) magnetite-alumina, (B) silica-alumina, (C)*
230 *magnetite-silica.*

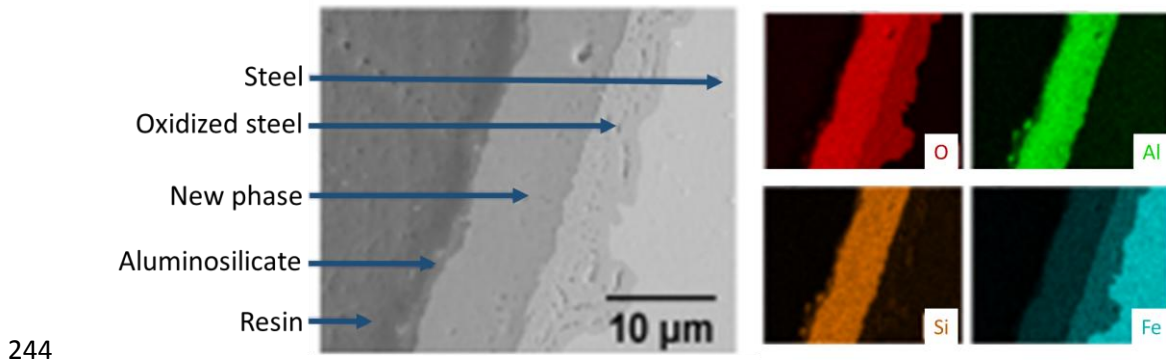
231

232 3.3. Role of metallic iron

233 From the previous experiments, the magnetite seems to have no role in the chemical reaction in
234 the system. Its solubility should be too low, as well as its dissolution kinetics, to release enough
235 soluble iron. In the secondary circuit, iron is present as magnetite, but large parts of the circuits are
236 made in carbon steel, which is subject to severe corrosion. As observed in literature at lower
237 temperature, this could change the iron reactivity.

238 To evaluate the impact of the iron availability, another experiment has been done with a carbon
239 steel coupon inside a suspension of alumina and silica. The SEM pictures and EDX maps of the cross
240 section of the coupon are shown in Figure 9. Contrary to the experiments with magnetite, in the XRD
241 analysis, the presence of berthierine ($\text{Fe}_2\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) has been detected. The cross section shows

242 (from left to right) the carbon steel covered by the native corrosion layer, then a thick layer of Fe-Al-
243 Si oxide (berthierine), and a thin layer of aluminosilicate covered by the resin.



245 *Figure 9. SEM pictures and EDX maps of a cross section of carbon steel/alumina/silica system*

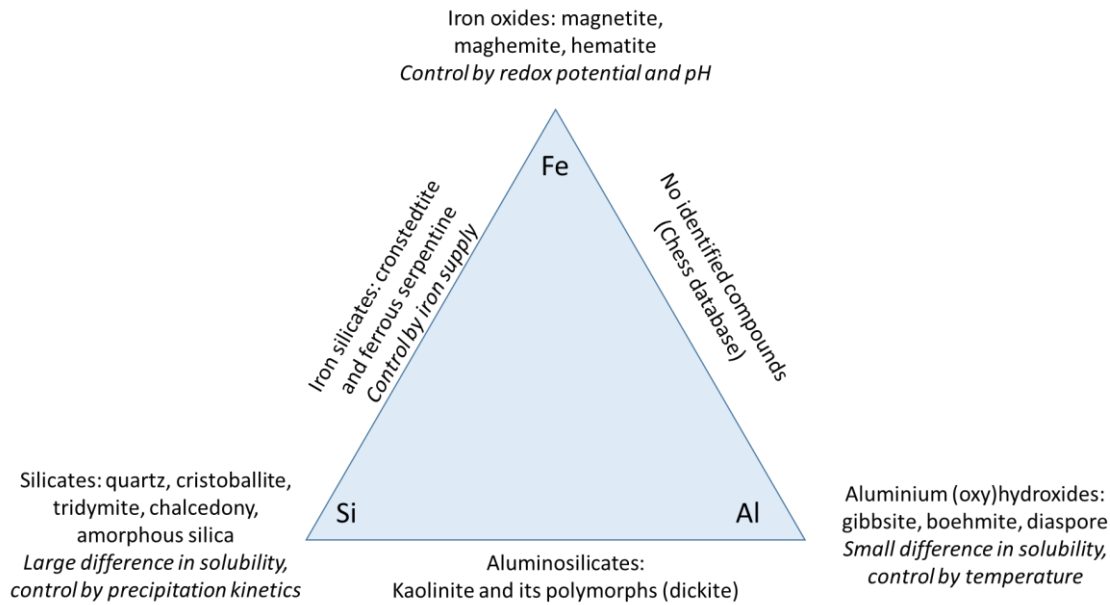
246 This observation is a proof that the oxidation of carbon steel release iron ions, which react with
247 dissolved silica and aluminum, or with the aluminosilicate layer already present at the interface to
248 form berthierine.

249

250 4. Discussion

251 Thermodynamic calculations have been made to simulate the evolution of the system consisting
252 in the mixture of magnetite, γ -alumina and amorphous silica. We did not consider the precipitation
253 of unlikely phases at this temperature such as corundum (α - Al_2O_3) that is supposed to not occur for
254 kinetic reasons. In the absence of silica, the only predicted reaction is the recrystallization of alumina
255 in stable hydroxides. In absence of magnetite, alumina and silica feed the precipitation of kaolinite or
256 its polymorph (dickite). In the absence of alumina, Fe-silicates (cronstedtite and Fe-serpentine)
257 constitute the stable secondary phases. In the ternary system, the calculations predict the formation
258 of iron phyllosilicates at the expense of the starting oxides. Figure 10 summarizes the diversity of
259 predicted stable parageneses depending on the starting oxides considered.

260



262

263

264

Figure 10: Predicted stable phases in the system Al_2O_3 - SiO_2 - Fe_3O_4

265

266

267

268

269

270

271

272

273

274

275

276

277

278

The conclusions based on Fig. 9 are well known by the geochemist in the Earth sciences. For example, the mineral “Chamosite-7Å” predicted in the ternary system is a proxy for berthierine, a 1:1-type layer silicate [20]. It was previously recognized (both theoretically and experimentally listed in the introduction) in investigations on underground storage of nuclear wastes, as the results of the interaction of metallic iron (waste container) and the clayed barrier (bentonite). From these studies, and our own simulations, the formation of berthierine or another iron phyllosilicate was expected in our ternary reference system, but it was not observed. By contrast, when using carbon steel as the source of iron the observation is consistent with the thermodynamic prediction. This discrepancy may be attributed to the low solubility of magnetite (the Fe source in our reference experiments). Indeed, the mineral reactions proceed by combination of aqueous species for nucleation and growth and at very low concentration of aqueous iron the precipitation of Fe-silicates is very slow, and these phases are improbable. In the presence of unstable metallic iron, the dissolution of iron, in true aqueous species or as colloids, is significant enough and does not limit the Fe-silicate growth.

279 Thus, the hard sludge environment is better modeled by a binary alumina-silica, magnetite being
280 inert. The following general sequence of reaction can be proposed: sedimentation of magnetite =>
281 confinement of the interstitial fluid => concentration of aqueous species such as aqueous silica and
282 alumina => sorption of Al on magnetite and/or growth of boehmite => reaction with aqueous silica to
283 form kaolinite. It is noticeable that kaolinite, a cl mineral, may form a resistant cement at the
284 microscopic scale.

285 In the presence of steel corrosion, the reaction is radically different. Metallic iron is not stable at
286 contact with water and the continual production of divalent iron, whose solubility is much higher
287 than that of magnetite, allows to overpass a threshold concentration what makes possible the
288 precipitation of berthierine. The berthierine precipitation at the contact of the corroded metal
289 constitutes the nucleation site for other aluminosilicate and is so the sink of silica. This affinity of
290 silica for corroded steel can be viewed as a competitive process of the hard sludge formation and we
291 can even speculate that, from this point of view, the corrosion of steel may potentially prevent the
292 formation of hard sludge.

293

294 **5. Conclusion**

295 Based on the industrial feedback and the laboratory works that has allowed the identification of
296 phenomena of agglomerations, this study aimed to identify and understand the mechanisms of
297 formation of hard sludge. The analysis of the suspension behavior and the decorrelation of the
298 parameters have generated a large number of information to explain the origins of the phenomenon
299 of agglomeration, which can be linked to the formation of hard sludge in the steam generators.

300 The analysis, correlation and comparison of these results allow not only to clearly identify this
301 phenomenon of agglomeration but also to deduce the mechanism. The in-depth analyses of the
302 samples have shown that the agglomeration of the powders is the consequence of the formation of a
303 cement that binds and traps the particles. This cement has been identified as being exclusively

304 kaolinite when magnetite is the iron-bearing solid. This cement is denser towards the surface of the
305 particles it traps. The orientation of kaolinite crystals suggests that part of the cement is formed on
306 the surface of the particles (magnetite and boehmite) by crystal growth, while the other, less dense,
307 part is formed by sedimentation and/or coagulation of kaolinite. Once formed, the kaolinite cement
308 tends to densify over time. Although this kaolinite cement is dependent on the presence of
309 aluminum and silicon, it is independent of the presence of magnetite. Furthermore, the experiments
310 have shown that if they do not react together to form an aluminosilicate, these two species may still
311 contribute to the densification of deposits. In the case of aluminum, by filling the porosities of the
312 magnetite in forming diasporite, and, in the case of silicon, by forming a compact gel around the
313 particles of magnetite. In addition to the identification of phases favoring agglomeration, the growth
314 of hydroxide of aluminum on the surface of the magnetite highlights the reactivity of aluminum
315 versus magnetite. Whereas magnetite seems inert to cement, it is not inert towards aluminum,
316 which once on the surface of the magnetite, can be a growth site for kaolinite cement.

- [1] B. Lanson, S. Lantenois, P. A. van Aken, A. Bauer et A. Plançon, «Experimental investigation of smectite interaction with metal iron at 80 °C: Structural characterization of newly formed Fe-rich phyllosilicates,» *American Mineralogist*, vol. 97, pp. 864-871, 2012.
- [2] S. Lantenois, B. Lanson, F. Muller, A. Bauer, M. Jullien et A. Plançon, «Experimental Study of Smectite Interaction with Metal Fe at Low Temperature: 1. Smectite Destabilization,» *Clays and Clay Minerals*, vol. 53, pp. 597-612, 2005.
- [3] R. Mosser-Ruck, M. Cathelineau, D. Guillaume, D. Charpentier, D. Rousset, O. Barres et N. Michau, «Effects of Temperature, pH, and Iron/Clay and Liquid/Clay Ratios on Experimental Conversion of Dioctahedral Smectite to Berthierine, Chlorite, Vermiculite, or Saponite,» *Clays and Clay Minerals*, vol. 58, pp. 280-291, 2010.
- [4] M. Perronnet, M. Jullien, F. Villiéras, J. Raynal, D. Bonnin et G. Bruno, «Evidence of a critical content in Fe(0) on FoCa7 bentonite reactivity at 80 °C,» *Applied Clay Science*, vol. 38, pp. 187-202, 2008.
- [5] M. Osacky, V. Sucha, A. Czimerova et J. Madejov, «Reaction of smectites with iron in a nitrogen atmosphere at 75 °C,» *Applied Clay Science*, vol. 50, pp. 237-244, 2010.
- [6] S. Kaufhold, A. Hassel, D. Sanders et R. Dohrmann, «Corrosion of high-level radioactive waste iron-canisters in contact with bentonite,» *Journal of Hazardous Materials*, vol. 285, pp. 464-473, 2015.
- [7] C. Rivard, M. Pelletier, N. Michau, A. Razafitianamaharavo, I. Bihannic, M. Abdelmoula, J. Ghanbaja et F. Villiéras, «Berthierine-like mineral formation and stability during the interaction of kaolinite with metallic iron at 90 °C under anoxic and oxic conditions,» *American Mineralogist*, vol. 98, pp. 163-180, 2013.
- [8] P. D. Svensson et S. Hansen, «Redox Chemistry in Two Iron-Bentonite Field Experiments at Äspö Hard Rock Laboratory, Sweden: An XRD and Fe K-Edge XANES Study,» *Clay and Clays Minerals*, vol. 61, pp. 566-579, 2013.
- [9] R. Wolfe et H. Feldman, «Steam generator management program: PWR steam generator top-of-tubesheet denting,» EPRI Rep., no. 3002002197, 2014.
- [10] H. Feldman, «Steam generator management program: assessment of the effect of deposit removal frequency on sludge management,» EPRI Rep. 1025127, 2012.
- [11] R. Fernandez-Saavedra, M. Gomez-Mancebo, M. Fernandez-Dias et D. Gomez-Briceno, «Role of aluminum and silicon species in the formation of hard sludge on the secondary side of PWR steam generators: Potential geopolymers contribution,» *Progress in Nuclear Energy*, vol. 118, p. 103136, 2020.
- [12] M. Vepsäläinen, «Deposit formation in PWR steam generators,» Research report VTT (VTT-R-

00135-10), 2010.

- [13] T. Dorsch, «Chemo-physical characterization on steam generator hard sludge particles,» AREVA Technical Rep. PTCC-G/2014/en/0081, 2014.
- [14] C. Turner, «Factors affecting the consolidation of steam generator sludge,» AECL report (AECL-10759), 1993.
- [15] C. Turner, «Physical and chemical factors affecting sludge consolidation,» AECL Technical Report (AECL611674), 1997.
- [16] L. Million-Picaillon, «Interactions magnétite-Al(III)-silice dans les conditions physico-chimiques des générateurs de vapeur des centrales nucléaires,» PhD, University of Toulouse, 2014.
- [17] K. Beal, L. Million-Picallion, G. Lefèvre, G. Berger, S. Delaunay, C. Goujon et J.-L. Bretelle, «Formation and Consolidation of Hard Sludge under Secondary Circuit Conditions,» chez *Nuclear Plant Chemistry Conference*, Brighton, 2016.
- [18] J. Van der Lee et L. De Windt, «CHESS Tutorial and Cookbook. Updated for version 3.0. Users Manuals,» Ecole des Mines de Paris, Fontainebleau, France, 2002.
- [19] E. Girel, A. Cabiac, A. Chaumonnot, M. Besson et A. Tuel, «Selective Carbon Deposition on gamma-Alumina Acid Sites: toward the Design of Catalyst Supports with Improved Hydrothermal Stability in Aqueous Media,» *ACS Applied Materials & Interfaces*, vol. 12, pp. 13558-13567, 2020.
- [20] E. Hornibrook et F. Longstaffe, «Berthierine from the lower cretaceous clearwater formation, Alberta, Canada,» *Clays Clay Minerals*, vol. 44, pp. 1-21, 1996.
- [21] R. Fernández-Saavedra, «Hard sludge and denting in the secondary side of PWR steam generators,» chez *Nuclear Plant Chemistry Conference*, Sapporo, 2014.

319

320

321

322