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Constraints on silicates formation in the Si-Al-Fe system: Application to hard deposits in steam generators of PWR nuclear reactors

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Introduction: The hydrothermal crystallization of silicates phases in the Si-Al-Fe system may lead to industrial constraints that can be encountered in the nuclear industry in at least two contexts: the geological repository for nuclear wastes and the formation of hard sludges in the steam generator of the PWR nuclear plants. In the first situation, the chemical reactions between the Fe-canister and the surrounding clays have been extensively studied in laboratory [1-7] and pilot experiments [8]. These studies demonstrated that the high reactivity of metallic iron leads to the formation of Fe-silicates, berthierine like, in a wide range of temperature. By contrast, the formation of deposits in the steam generators of PWR plants, called hard sludges, is a newer and less studied issue which can affect the reactor performance.

Experiments: We present here a preliminary set of experiments reproducing the formation of hard sludges under conditions representative of the steam generator of PWR power plant: 275°C, diluted solutions maintained at low potential by hydrazine addition and at alkaline pH by low concentrations of amines and ammoniac. Magnetite, a corrosion by-product of the secondary circuit, is the source of iron while aqueous Si and Al, the major impurities in this system, are supplied either as trace elements in the circulating solution or by addition of amorphous silica and alumina when considering confined zones. The fluid chemistry is monitored by sampling aliquots of the solution. Eh and pH are continuously measured by hydrothermal Cormet© electrodes implanted in a titanium hydrothermal reactor. The transformation, or not, of the solid fraction was examined post-mortem. These experiments evidenced the role of Al colloids as precursor of cements composed of kaolinite and boehmite, and the passivation of amorphous silica (becoming unreactive) likely by sorption of aqueous iron. But no Fe-bearing was formed by contrast to many published studies on the Fe-clay interactions in the nuclear waste storage, and by contrast with basic thermodynamic predictions.

Conclusion: The Fe-clays and steam generators contexts imply relatively close aqueous environments: hydrothermal, reduced, diluted, neutral to slightly alkaline. The main difference is the status of iron: ferric/ferrous (magnetite) in the steam generators, metallic in the Fe-clay experiments. The concentration of aqueous iron when supplied by magnetite is low and does not allow its incorporation in secondary phases. By contrast, aqueous ferrous iron released by the corrosion of steel is not limited by the source, rather by the sink, and produces Fe-rich silicates. This example illustrates the discrepancy between complex mineral reactions and oversimplified predictions when sorption/passivation and nucleation/growth constraints are ignored.

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