EXPERIMENTAL AND COMPUTATIONAL ACHIEVEMENTS ON THE IMMOBILIZATION OF HIGH-LEVEL NUCLEAR WASTES

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Safe and long-term stable high-level nuclear waste confinement is a goal that seems far from been achieved, like in the case of the immobilization of molibdenum radionuclides. Here a state of the art of problems and challenges, where the synergy of experiments and modelling arises as the best strategy

Risultati sperimentali-computazionali nell'immobilizzazione di scorie nucleari ad alta radioattività
Il confinamento, sicuro e a lungo termine, di scorie nucleari ad alta radioattività è un obiettivo difficile da raggiungere. Una panoramica delle problematiche e delle possibili soluzioni ha portato la comunità scientifica a rivolgersi a un metodo sinergico computazionale-sperimentale.

High-level nuclear wastes (HLW) outcome from the production cycle of nuclear waste energy. They consist of liquid solutions and dredging sludge containing long-life radionuclides and, although barely constitute the 5% wt. of the total nuclear wastes, HLW emit the 98% of total radiation.

After the II World War, the countries that developed the nuclear technology for defense purposes (UK, France, USSR and USA) started to elaborate strategies for nuclear waste processing and disposal. The most effective and advanced procedure of spent fuel processing, which is now-a-days operated at the industrial scale, consists of 3 phases: i) recovery of residual U and Pu by organic solvents separation[1,2,3], ii) incineration of the remaining organic solutions which contain HLW and iii) chemical immobilization of solid state HLW by vitrification into borosilicate glass matrixes[4,5]. Each country that processes HLW have adopted its specific set of borosilicate compositions, which are optimized on the basis of HLW composition, for example R7T7 French glass contains Ca[6], while the British MW glass contains Mg[4].

Although oxide-based glasses were found to be more effective in HLW confinement than metals or zeolites, they are metastable phases that naturally undergo irreversible transformation into stable crystalline phases on the long-term period. This kind of alteration is particularly expected for radionuclides having low solubility in borosilicate glasses, like Mo, and are known to compromise mechanical properties of the matrix, undermining the confinement power of the glass. Further alterations mechanisms, expected in deep geological disposal environment, are self-irradiation and self-heating caused by short-lived fission products (like ^{90}Sr and ^{137}Cs)[7], and water chemical attack. Borosilicate glasses have been elected among oxide-based glasses because, beyond a high load capacity of HLW[4], they exhibit a "self-healing" power that prevents total matrix degradation. Actually, the presence of Si and Al ensures passivation to hydrolysis by the formation of a silicate gel layer[8].

Although the aforementioned alteration mechanisms were widely understood by means of experimental investigations, modeling arose as an essential investigation protocol to understand and predict HLW glass behavior. Models are validated by comparing the obtained numerical data with experimental results on reference samples, like billions years old obsidians or non-radioactive homologous. The mutual employment of experimental and calculated data results in the so-called *computational-experimental approach*. This approach is essential to study the behavior on long-time scale of HLW glasses, which cannot be reliably investigated in the short-time scale of laboratories, or to predict structural arrangement in function of the composition, to guide experimentalists in the design of novel and more effective nuclear glass compositions.

Our research group tuned the synergetic computational-experimental approach[9] in order to study how to immobilize Mo radioisotopes in glass matrixes. In fact, Mo release is caused by Na-Mo chemical zoning, which induces the crystallization of Na_2MoO_4 phase undermining the whole glass mechanical durability. Moreover, Na_2MoO_4 is highly soluble in water, further increasing the probability of long-term and high-level environment contamination. With the aim to study how Na-Mo chemical zoning depends on composition, we adopted solid state Nuclear Magnetic Resonance as the experimental reference technique.

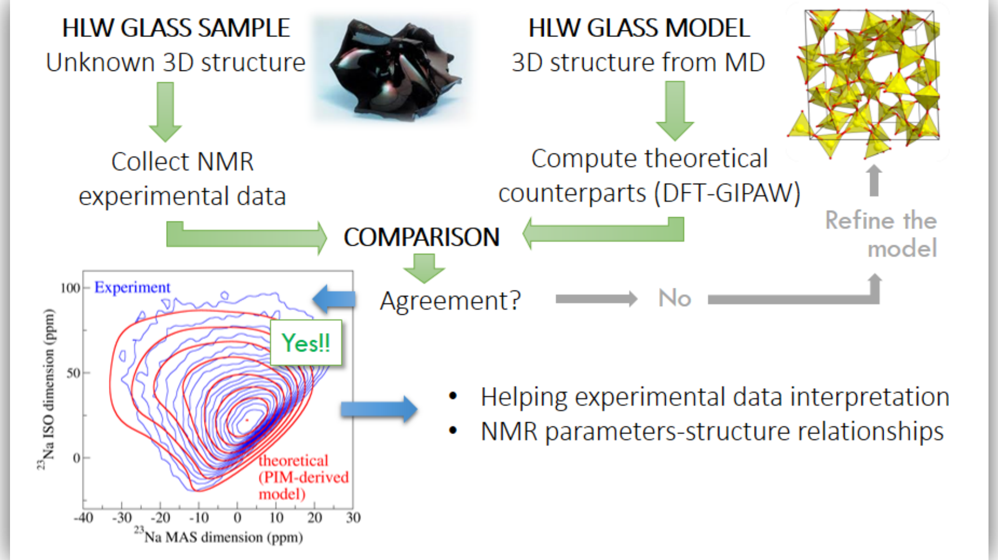

Fig. 1
The synergetic experimental-computational approach for structural charachterization

Fig. 1 explains how our approach works. For given samples, we collect NMR spectra and perform Neutron Diffraction (ND) analysis. At the same time, we generate structural models with various molecular dynamics protocols and calculate ND and NMR counterparts on the structural models. Whether the experimental data and the theoretical counterpart do not agree, we exclude or refine wrong protocols, depending on the seriousness of the disagreement, and repeat the comparison until a good agreement is found. For example, Fig. 2 shows the simulated Mo environment in a Ba-Na silicate glass: tetrahedral coordination and bond length agree with previous experimental findings[10]. Many other comparisons on structural parameters confirmed the validity of the computational protocol, thus the next step will be NMR spectra interpretation and the elaboration of NMR-structure relationships. In summary, in this approach, experiment verifies the theory and theory explains the experiments.

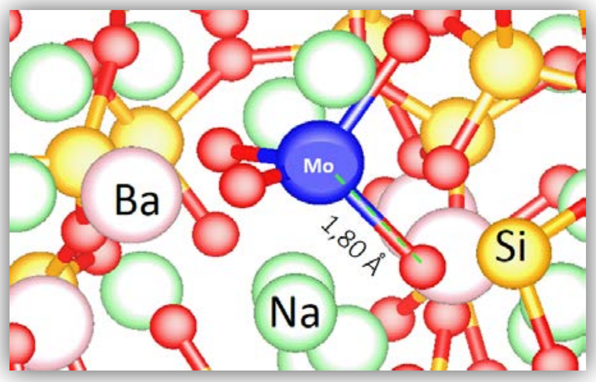

Fig. 2
Simulation of Mo environment: Mo-O bond length and tetrahedral coordination geometry

The potentiality of this method is to achieve an *in-silico* determination of a set of compositions that minimize Na-Mo chemical zoning and, in turn, maximize Mo immobilization power. The *in-silico* procedure is ways cheaper and less time-demanding than direct experiments. Moreover, it will be possible to provide experimentalists with spectroscopic fingerprints of strategic structural features that must be monitored in glass samples, like Na-Mo clustering and extra-framework cation intermixing.

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