CHERNE 2018 - 14th Workshop on European Collaboration in Higher Education on Radiological and Nuclear Engineering and Radiation Protection

Fluorapatite as immobilization matrix for nuclear waste

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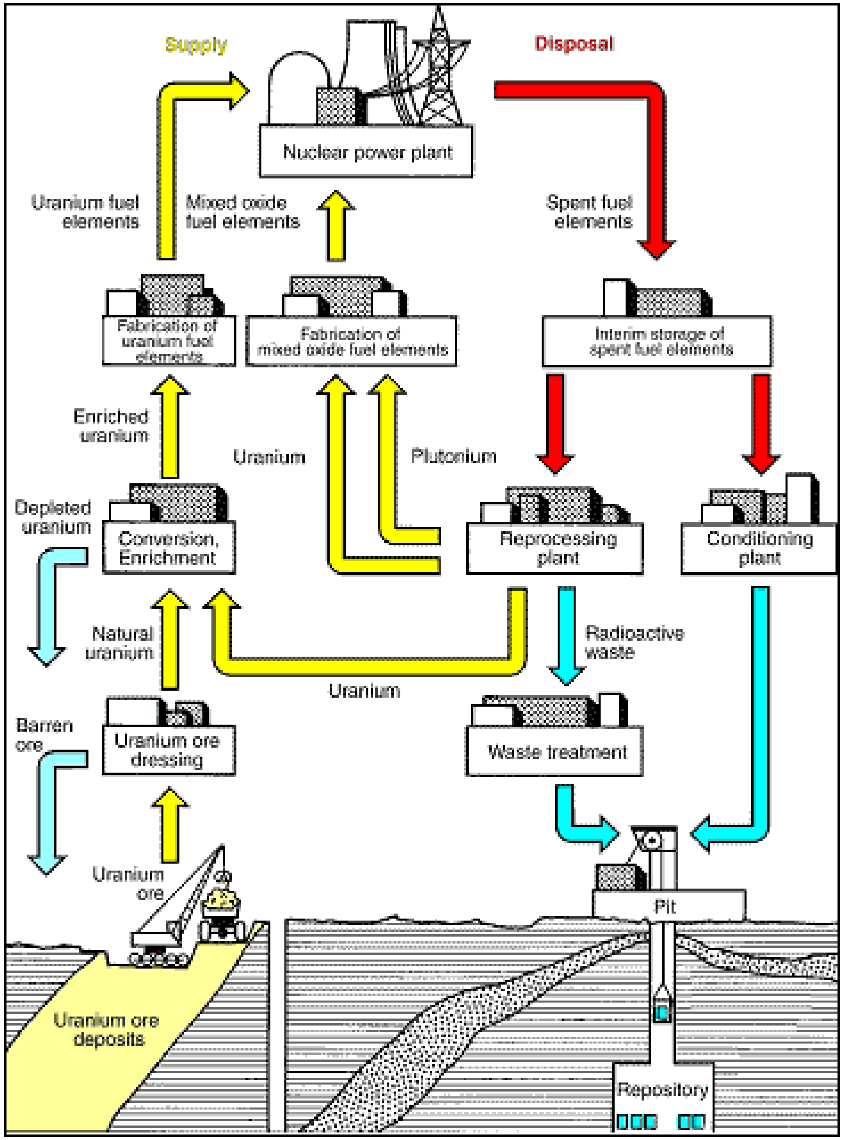
Closed Nuclear Fuel Cycle

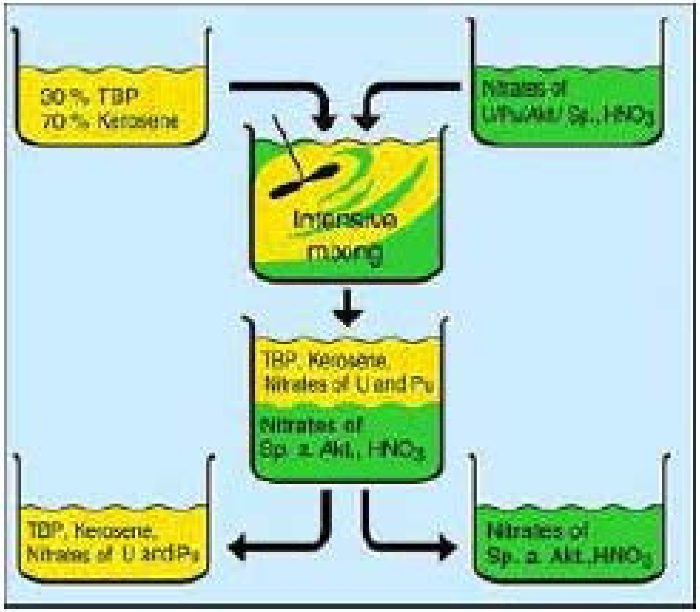


Sustainability – Acceptability

- Recycling of reusable material
- Better waste management
- Radiotoxicity reduction
- Proliferation resistance

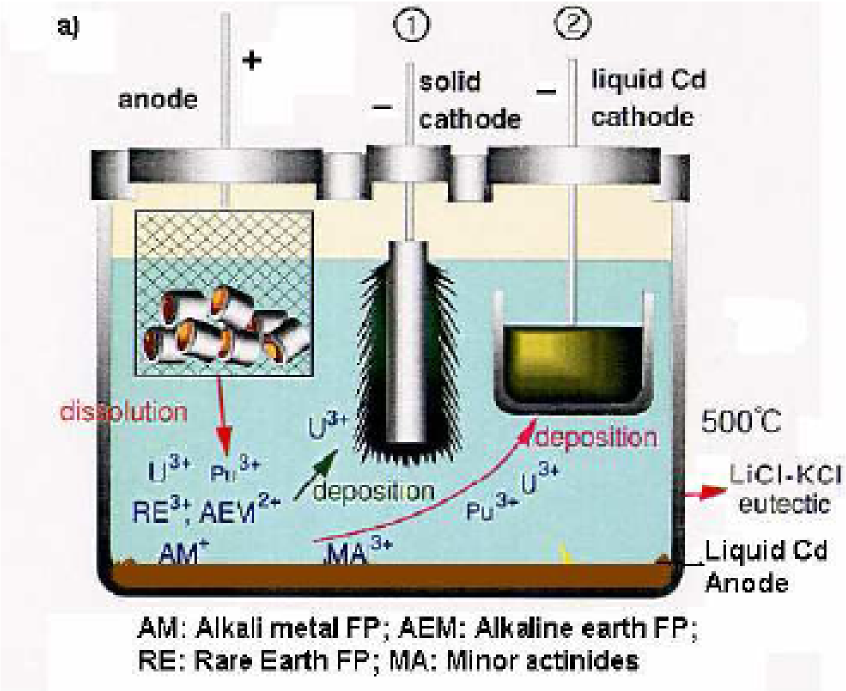
Reprocessing of Spent Nuclear Fuel

Hydrometallurgical reprocessing



Aqueous solutions
containing metals nitrates

Pyrometallurgical reprocessing



Chloride / Fluoride salts

Conditioning of nuclear waste

CONDITIONING PROCESSES → to convert radioactive waste materials into stable solid forms suitable for transportation, storage and final disposal

CEMENTATION/ VITRIFICATION → Insoluble solid forms able to prevent dispersion to the surrounding environment

- Identification of a suitable matrix material – such as cement, bitumen, polymers or borosilicate glass, depending on the type of waste being conditioned;
- Immobilization of the waste through mixing with the matrix material;
- Packaging the immobilized waste in metal drums, metal or concrete boxes or containers, or copper canisters.

A more sophisticated approach is incorporating wastes into the crystal structure of **NATURAL MINERALS** which are geochemically stable:

- Synrocs;
- Ceramics;
- Glass-ceramic composites;

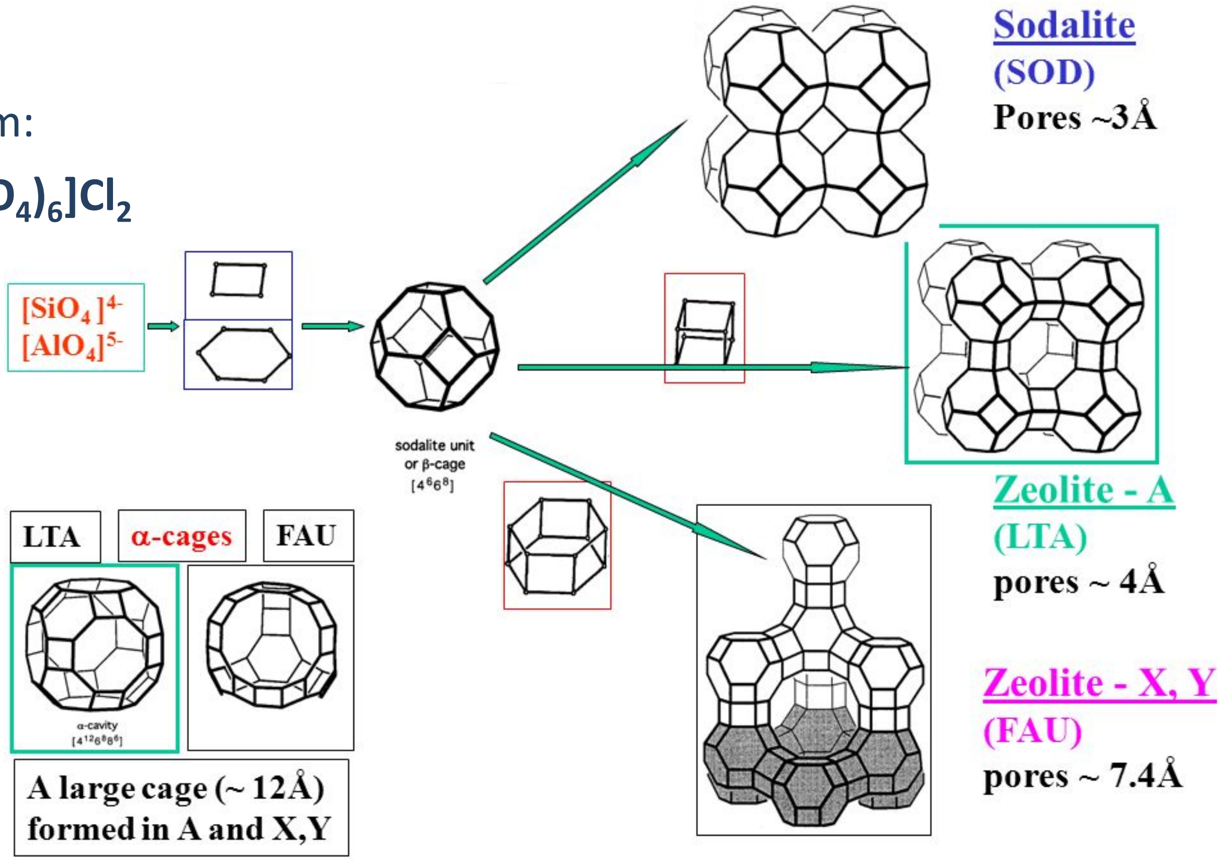
Pyrochemical reprocessing

↳ Chloride-containing radioactive wastes → Immobilization in Borosilicate glasses or Synroc-type ceramics not viable due to physico-chemical incompatibility

↓

Alternative wasteform:

Sodalite, $Na_8[(AlSiO_4)_6]Cl_2$
Zeolite A



Fluorapatite (FAP) as matrix for fluoride-containing waste coming from pyro-reprocessing

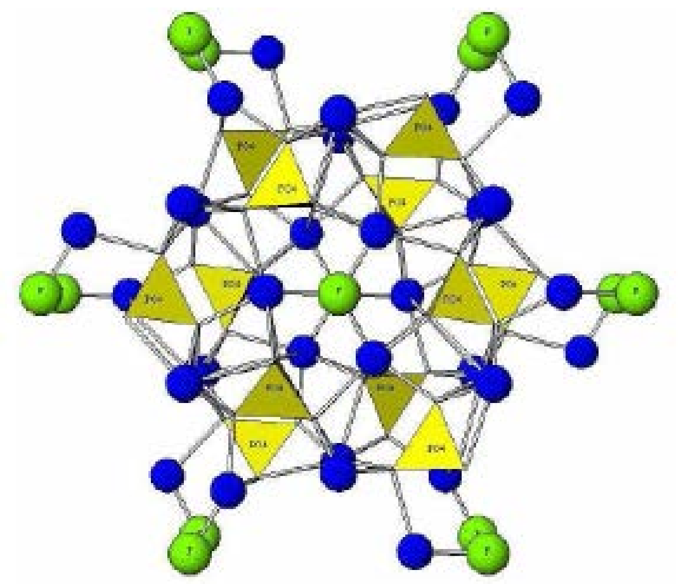
Chemical formula: $\mathbf{Ca_{10}(PO_4)_6F_2}$

Phosphate mineral:

- Hard crystalline solid
- Space group $P6_3/m$

Chemical physical properties:

- stability
- able to accommodate a large variety of cations (mono-, bi- and trivalent) and anions in non-stoichiometric compositions
- strongly insoluble in water ($K_{ps} = 8,1*10^{-121}$)
- highly resistant to radiation-induced damage



$$3Ca_3(PO_4)_2 + CaF_2 \rightarrow Ca_{10}(PO_4)_6F_2$$

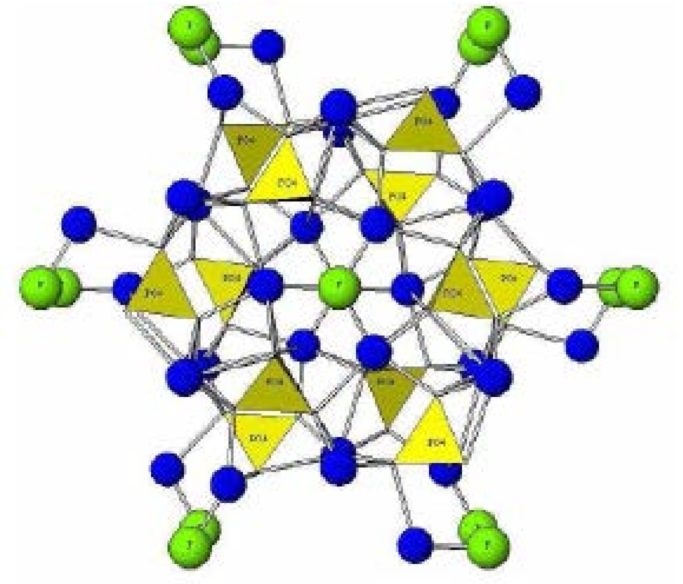
Waste in the form of **fluoride** (SrF_2)

$$3Ca_3(PO_4)_2 + SrF_2 \rightarrow Ca_9Sr_1(PO_4)_6F_2$$

R. Fábián, I. Kotsis, P. Piltér, *Hungarian Journal of Industrial Chemistry* 27 (1999), p. 259-263;
P. Innocente, *Studio di matrici per il confinamento di prodotti di fissione: sintesi allo stato solido e caratterizzazione di fluoroapatiti*, M. Sc. Thesis, 2007;

FAP as matrix for fluoride-containing waste coming from pyro-reprocessing

- Synthesis of FAP matrix with Sr substituted to Ca at different % by solid state reaction



- Characterization of the Sr-FAP by:
  - ✓ XRD → Rietveld refinement
  - ✓ Raman
  - ✓ SEM-EDS
  - ✓ EPR

Sr-FAP synthesis

$3Ca_3(PO_4)_2 + SrF_2 \rightarrow Ca_9Sr_1(PO_4)_6F_2$ up to Sr 10%at.

Thermal treatment: 1000°C, 2 h, under upstream of SrF_2

Highest cations substitution → Highest volume reduction

$Ca_3(PO_4)_2 \rightarrow Sr_3(PO_4)_2$

Synthesis of Sr phosphate by:

- wet chemical route

  $3Sr(NO_3)_2 + 2(NH_4)_2HPO_4 + 2NH_3 \rightarrow Sr_3(PO_4)_2\downarrow + 6NH_4NO_3$

- solid state reaction

  $3SrCO_3 + 2(NH_4)_2HPO_4 \rightarrow Sr_3(PO_4)_2 + 2NH_4CO_3 + H_2O + CO_2$

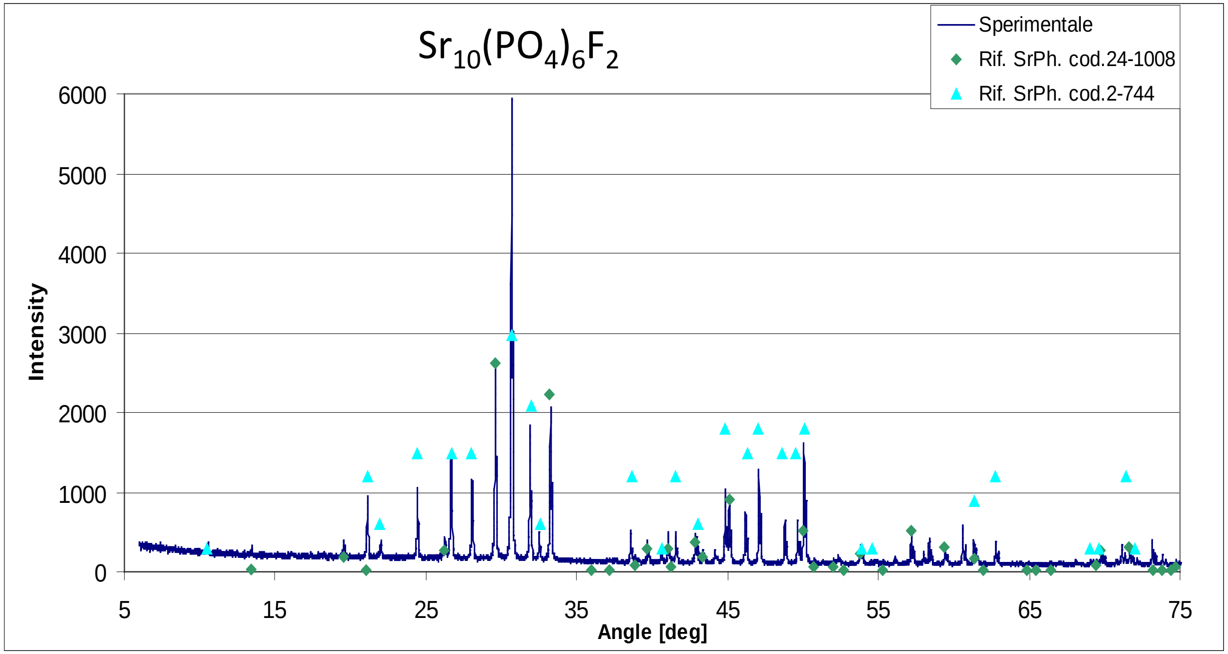
Literature synthesis evaluated:

60%at.: $2Sr_3(PO_4)_2 + Ca_3(PO_4)_2 + CaF_2 \rightarrow Ca_4Sr_6(PO_4)_6F_2$

73%at.: $2{,}1Sr_3(PO_4)_2 + 0{,}9Ca_3(PO_4)_2 + SrF_2 \rightarrow Ca_{2,7}Sr_{7,3}(PO_4)_6F_2$

100%at.: $3Sr_3(PO_4)_2 + SrF_2 \rightarrow Sr_{10}(PO_4)_6F_2$

Thermal treatment at 1000°C, 2 h, under **Argon** flow (20 l/h)



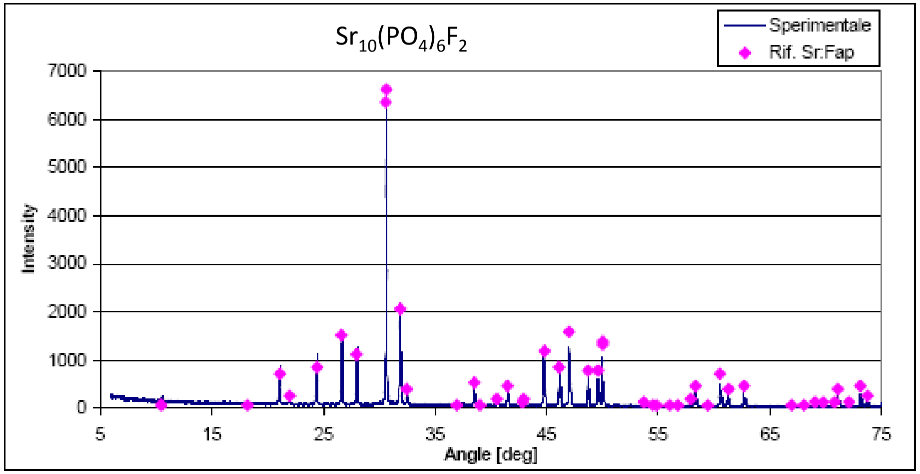
- Inhomogeneity in ethanol
- Insufficient upstream of SrF_2
- T = 1000°C not enough to obtain FAP
- Strontium phosphate reactive but kinetic reaction too slow

Sr-substituted fluorapatite

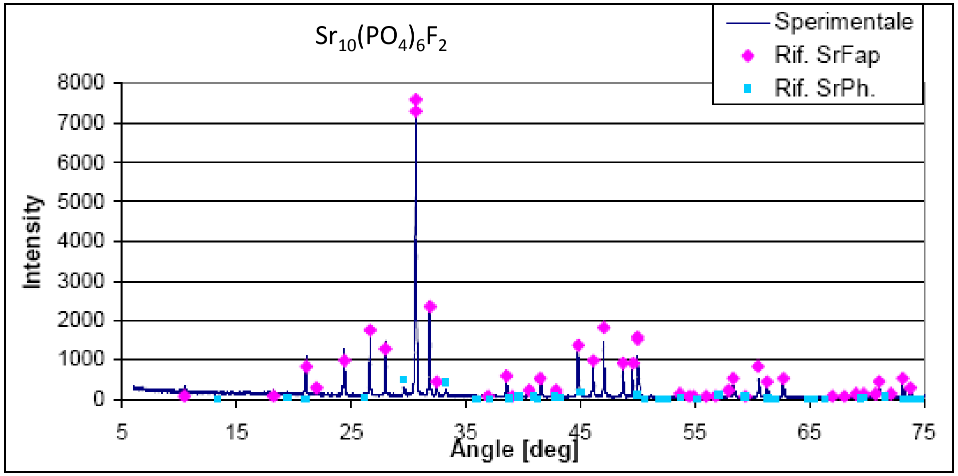
Thermal treatment at 1250°C, 7 h, in **air**

- Sr:Fap has been obtained
- Mixed Ca-Sr:FAP phases with %at. lower than those expected
- Some traces of Sr phosphate

Thermal treatment at 1350°C, 5 h, in **air**

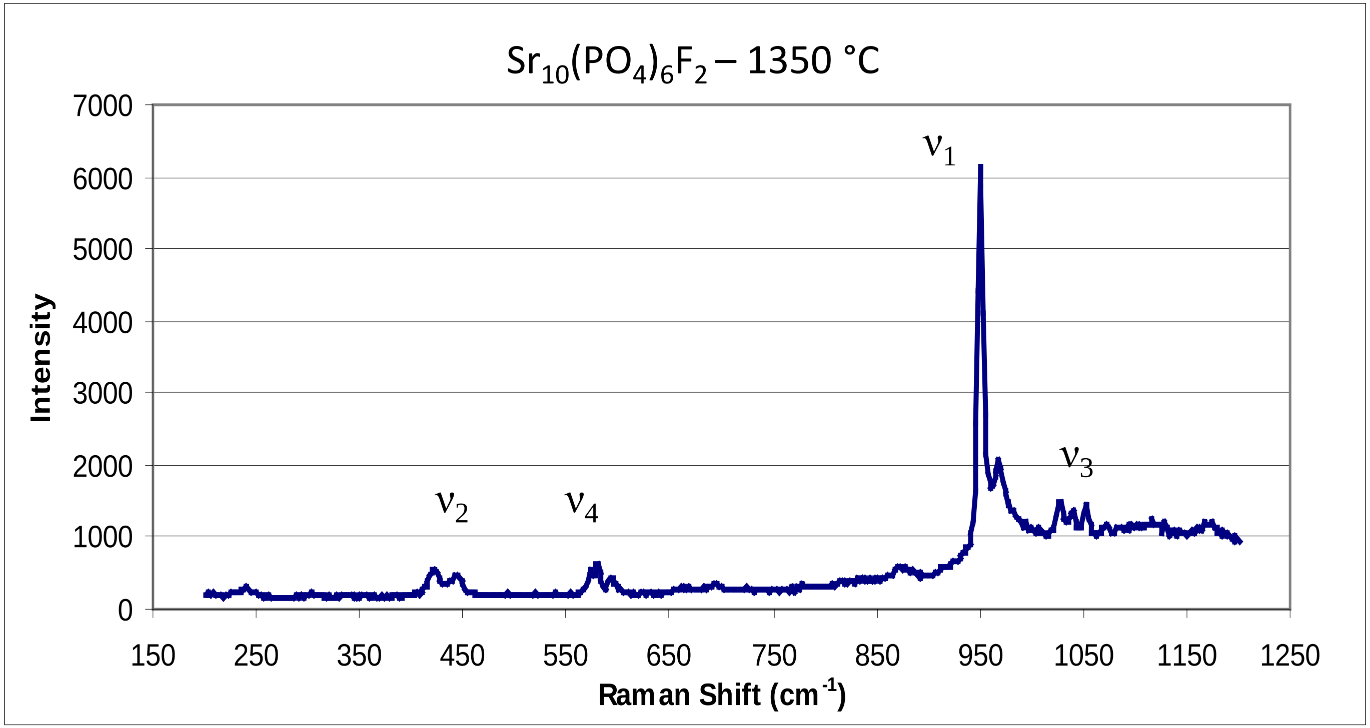


Hyperstoichiometric SrF_2



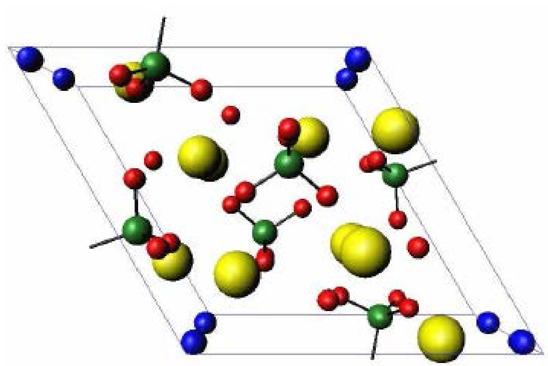
Stoichiometric SrF_2

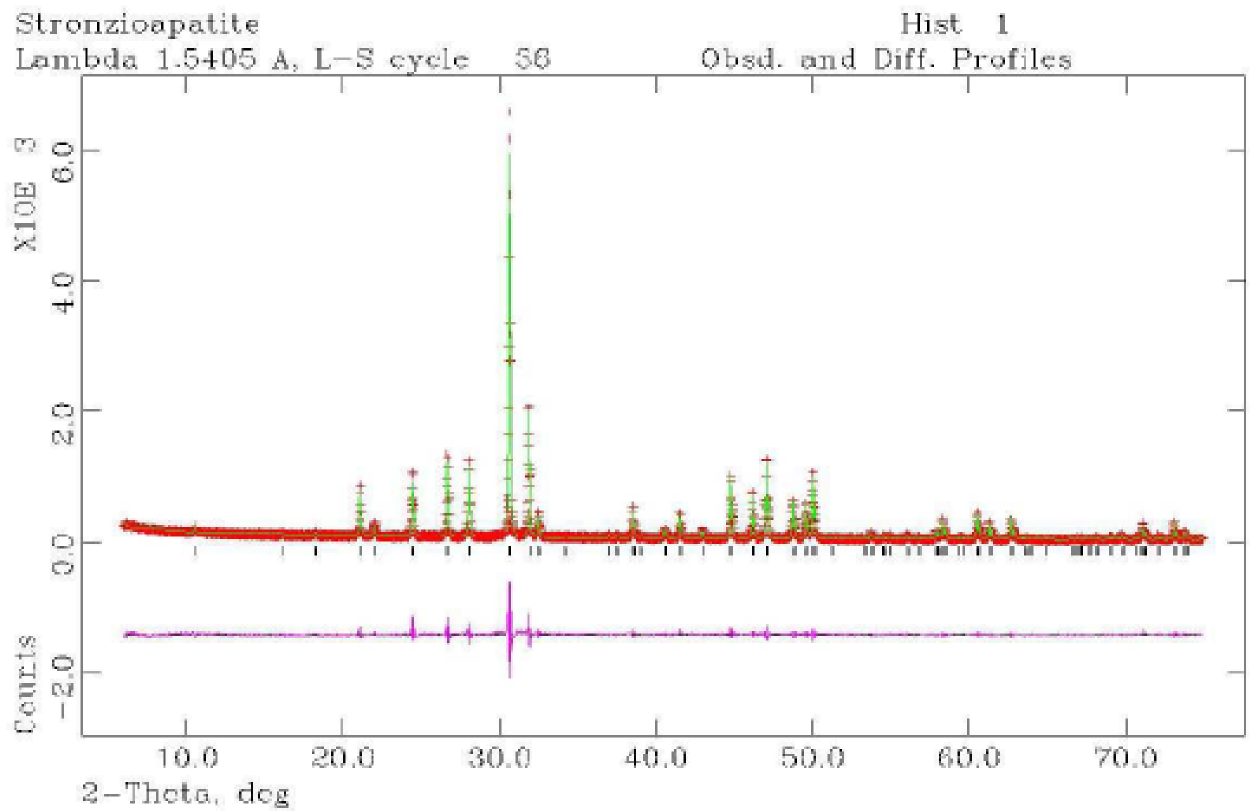
Raman spectroscopy



ν_2=415-440 cm^{-1} ν_4=572-590 cm^{-1} ν_1 = 951 cm^{-1} ν_3= 1025-1050 cm^{-1}

Rietveld Refinement (RR)





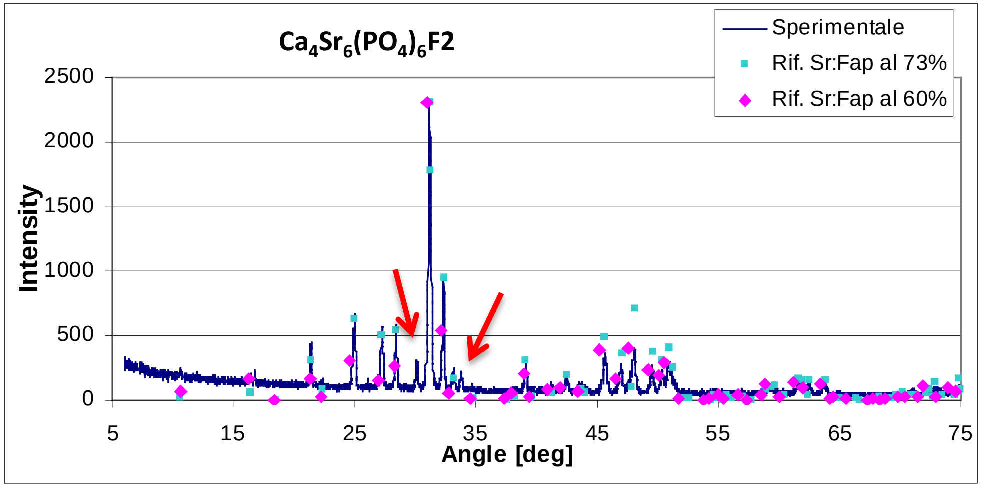
$R_{wp} \approx 10\%$

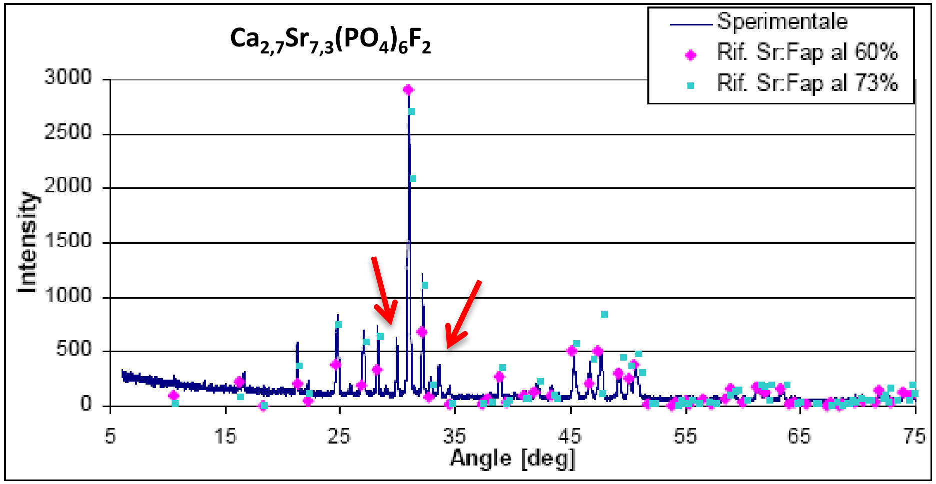
Cell Parameters							
a [Å]		*c* [Å]		*V* [Å^3]		*ρ* [g/cm^3]	
Reference	RR	Reference	RR	Reference	RR	Reference	RR
9,7174	9,7219	7,2851	7,2853	595,75	596,33	4,14	4,13

A. C. Larson, R. B. Von Dreele, *General Structure Analysis System (GSAS)*, Los Alamos National Laboratory Report LAUR 86-748 (2004)

Sr-substituted fluorapatite

Thermal treatment at 1350°C, 5 h, in **air**

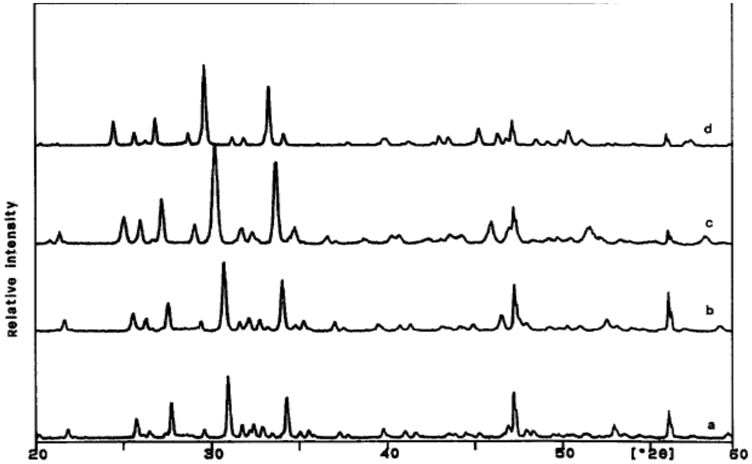




- Unidentified peaks/phases at 2θ = 30-34°
- Formation of Ca-Sr:FAP phases

Main peaks of mixed Ca-Sr posphate in the 2θ range 30-34°

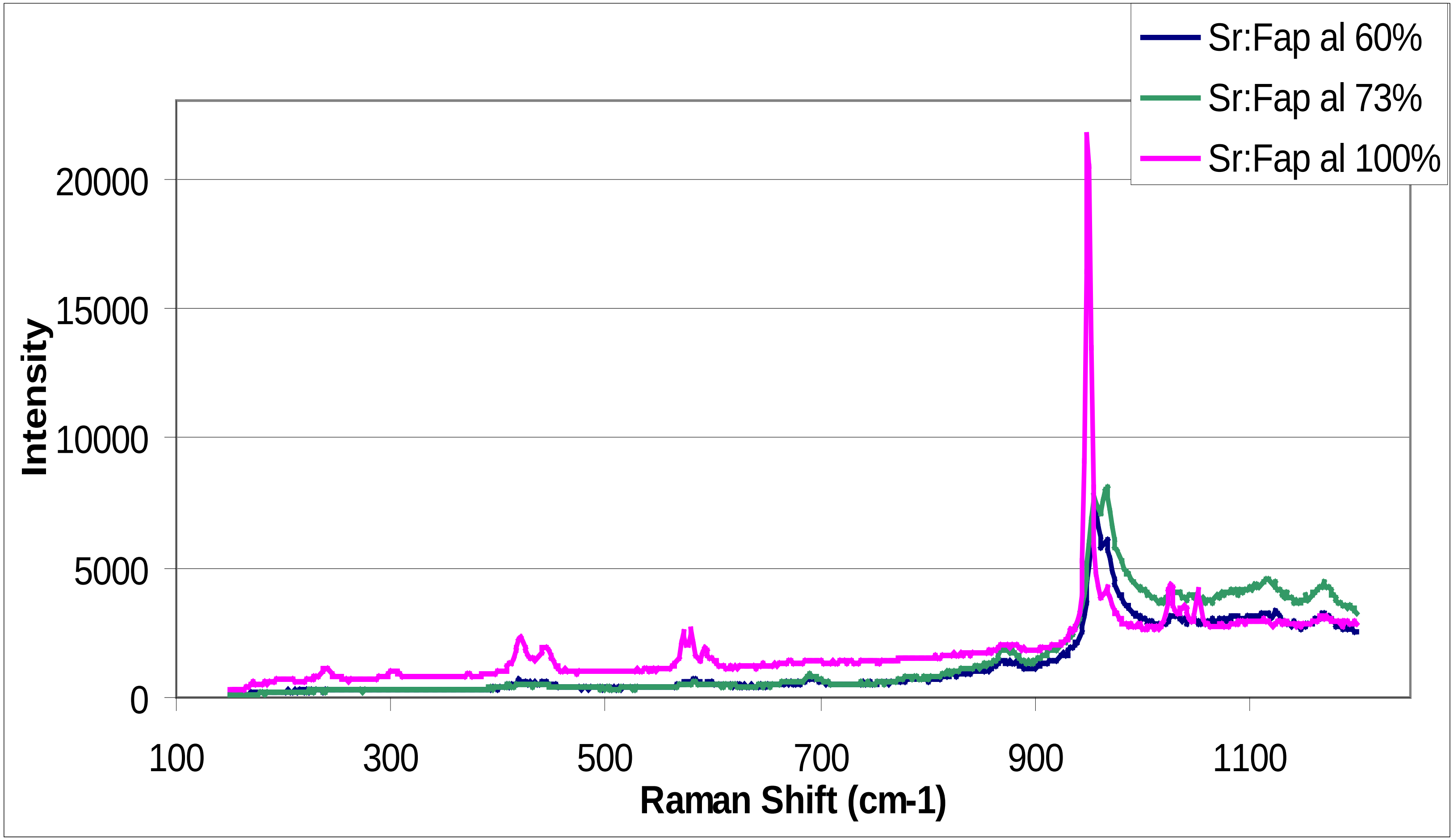
Lower Sr substitution



A. Bigi, E. Foresti, M. Gandolfi, M. Gazzano, N. Roveri, Journal of Inorganic Biochemistry 66 (1997), pag. 259-267

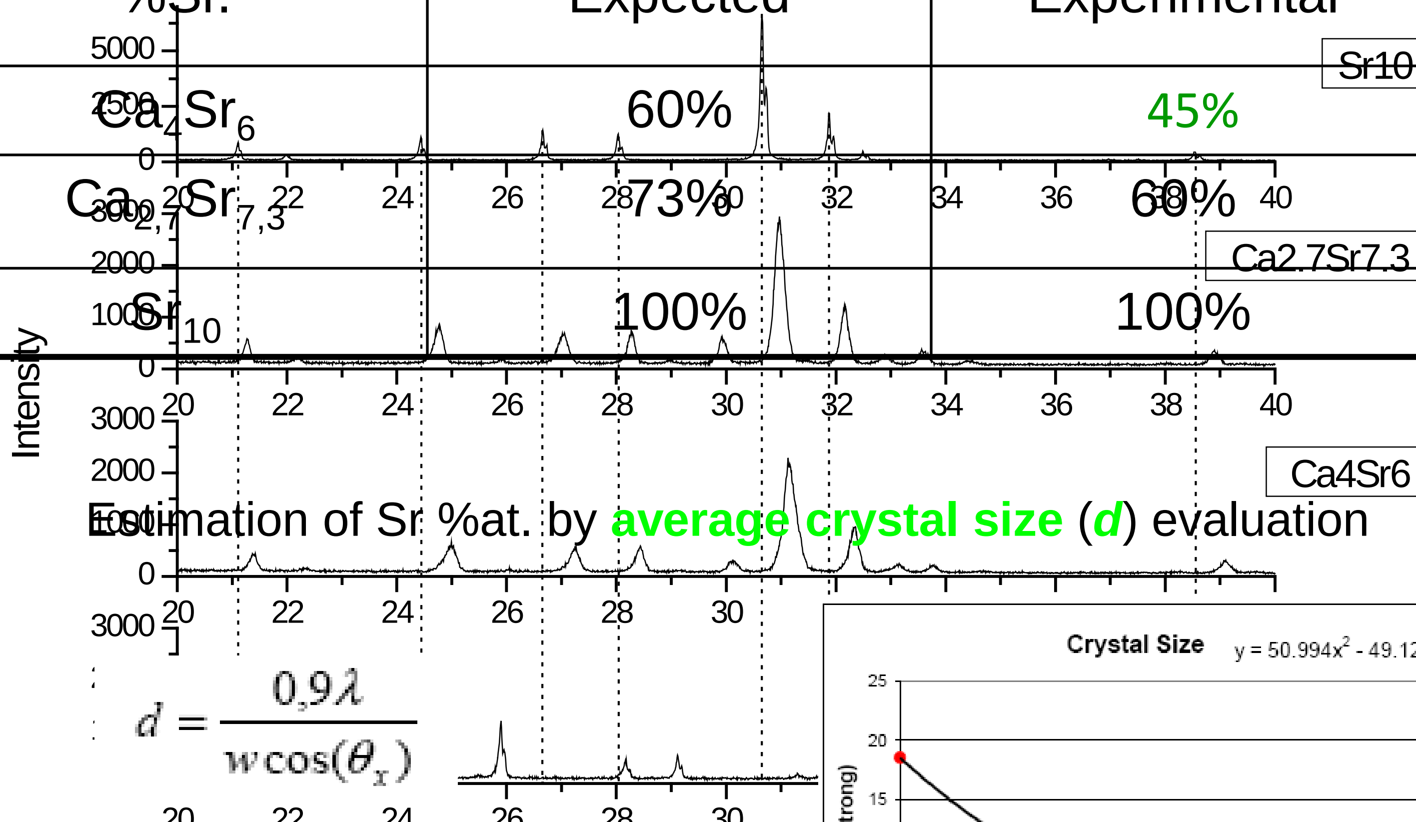
Sr-substituted fluorapatite

Comparison of raman spectra



Sr-substituted fluorapatite

%Sr.	Expected	Experimental
Ca_4Sr_6	60%	45%
$Ca_{2,7}Sr_{7,3}$	73%	60%
Sr_{10}	100%	100%

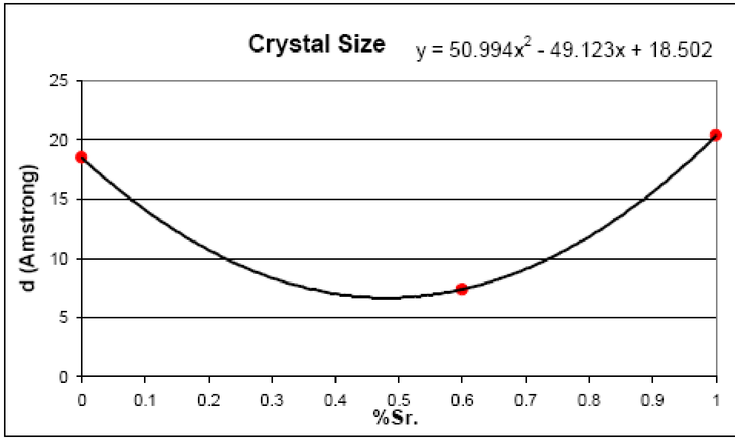


XRD

Estimation of Sr %at. by **average crystal size** (***d***) evaluation

$$d = \frac{0{,}9\lambda}{w\cos(\theta_x)}$$

- Lorentzian Fit of main peak
- Parabolic trend of ***d*** with respect to Sr%



Conclusions and future works

- Successful synthesis of fully substituted Sr:FAP by a solid state reaction at 1350°C for 5 h in air
- No need of inert atmosphere
- Important role of homogeneization step
- Important role of upstream to balance fluorine losses

- Optimization of synthesis of Ca-Sr:FAP
  - Better homogeneization
  - Use of hyperstoichiometric SrF2
  - Use of mixed Ca-Sr phosphate $Ca_{3-x}Sr_x(PO_4)_2$
- Leaching experiments to assess durability in water
- Study of FAP doped with lanthanides (Gd^{3+})


232.038
+2
+3
+4
Th
90
2-8-18-32-18-10-2
ank
Yo
238.029
+2
+3
+4
+5
+6
U
92
2-8-18-32-21-9-2