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Viability of the sustainable valorization of the dicalcium phosphate residues: towards the safe management of NORM residues (Abstract #97)

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1. Background and goal of the present work

Like many other industries, decommissioning a dicalcium phosphate production facility generates different waste streams. Generic wastes may include dismantled equipment, contaminated soil, a mixture of soil and sludge, scale, and other miscellaneous materials. Residues generated in the dicalcium phosphate production consist of **sludge (1)** of undissolved phosphate rock, SiO_2 and fluoride compounds such as CaF_2. When simultaneous calcium chloride production occurs at the same facility, another type of **sludge (2)** is formed, mainly composed of $Mg(OH)_2$ (Fig. 1).

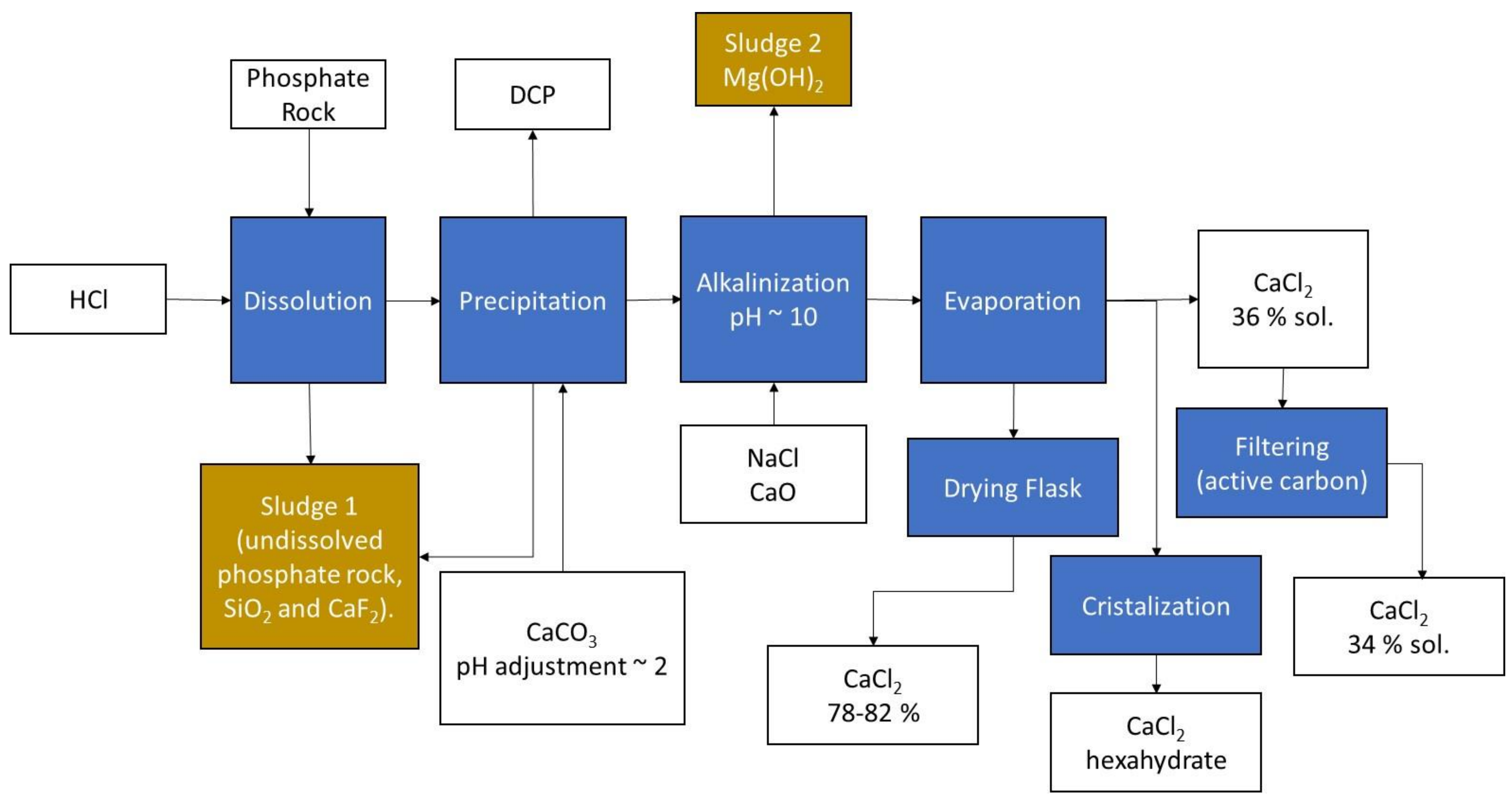

Fig. 1: Simplified diagram of the DCP production process [1].

The conventional dicalcium phosphate (DCF) production process involves reacting the phosphate rock with acid sulphuric to produce phosphoric acid. The original process was patented in 1917 describing the production of inorganic feed phosphates by digesting the phosphate rock with hydrochloric acid, leading to crystalline dicalcium phosphate as represented by the reactions [2]:

$$Ca10(PO_4)6F_2 + 18HCl \rightarrow 9CaCl_2 + CaF_2 + 6H_3PO_4 \quad (1)$$

$$H_3PO_4 + CaCO_3 \rightarrow CaHPO_4 + CO_2 + H_2O \quad (2)$$

Several methods and modifications are used to separate fluoride – an undesirable impurity in the production process; iron; aluminium; magnesium; manganese impurities, and silica.

Fluorspar is on the EU's Critical Raw Materials (CRMs) list and therefore is one of the materials considered crucial to Europe's economy. The CRMs form a solid industrial base, producing various goods and applications used in everyday life and high-tech industries. Reliable and unhindered access to certain raw materials is a growing concern within the EU and across the globe.

A critical aspect of the potential valorisation or recycling these residues comes from the presence of radionuclides. Among the radionuclides that may be present in the sludge are U-238, U-234, Th-230, Ra-226 and Pb-210. The IAEA Safety Standards No. SSG 60 (Section 6) elaborates on strategies for NORM residue management, including exemption and clearance [3]. In addition, the Safety Report N.º 49 addresses the Radiation Safety Basis for the Management of NORM Residues (Section 4) [4].

This work intends to study the viability of the valorisation of dicalcium phosphate residues by developing a methodology to evaluate the potential use of these residues as a source of CRMs and as secondary resources, for example, to manufacture sulphur polymer concretes. The material to be tested resulted from the decommissioning of a dicalcium phosphate production facility and comprise 20 to 30 tons of residues.

2. Methodology

2.1 Compile existing valorization processes with DCF residues

- Review existing valorization processes for DCF residues that demonstrate the potential and challenges of its use as CRMs sources or secondary mineral resources.
- Search in databases (Scopus and Web of Science) with a combination of the keywords: “Dicalcium Phosphate”, “NORM”, “Residues”, and “Valorization”.
- Relevant studies published between 2013 and 2023 were selected. All articles deemed eligible were successfully downloaded. The survey followed the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines and the PRISMA 2020 checklist to screen articles, extract information, and summarize relevant indicators. Further work will perform a descriptive synthesis and analysis of the data.
- Search in other databases (e.g. IAEA) for previous characterization works on Dicalcium Phosphate residues.

2.2 Characterization protocols of the DCF residues

- Develop a detailed characterization protocol:
  - Chemical characterization: metals (Al, Fe, Zn, Cd, Cr, As, Hg, Pb and Mg) and REEs (e.g. Y, La, Ce and Nd);
  - Radiological characterization: ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po;
  - Mineralogical characterization: X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM);
  - Particle size analysis and density;
  - Natural leaching tests;
  - Geotechnical and mechanical properties (laboratory-scale tests).

2.3 Possible applications as CMRs sources or secondary resources

- Expected ^{238}U, ^{234}U, ^{226}Ra, ^{230}Th, ^{210}Pb, and ^{210}Po in sludge (1) and in sludge (2);
- Tasks to de developed:
  - Develop methodology for the concentration of fluorite;
  - Removal of radionuclides (U-Th);
  - Recovery of existing phosphogypsum in the residues;
  - Extraction of critical elements;
  - And assessment of the viability of residues be incorporated into the manufacture of cement, concrete, geopolymers and filling material.

2.4 Define exposure scenarios and dose calculation

- Define potential exposure scenarios for potential developed products (e.g. application in construction works like pavements in highways and parking lots);
- Inclusion of the exposure routes and impact pathways in a LCA for the (re)use and/or recycle of the residues, for each exposure scenario, and according to the application;
- Dose calculation and verification of the compliance with the applied safety criteria in each considered situation [5, 6].

3. Conclusions

- Proposed work is under development: it is expected to finish the development of the characterization protocols soon to start the laboratory-scale tests.
- Described approaches to (re)use and/or recycle NORM residues are in line with the UN SDGs, particularly SDG 9 on industry, innovation and infrastructure, SDG 12 on responsible consumption and production and SDG 17 on partnerships for the goals.
- REE recovery is strongly linked to the production and consumption of renewable energy and energy efficiency (SDG 7), supported and linked to resource efficiency (SDG 8, SDG 9).
- Safety and environmental objectives are implicit in the proposed work, in alignment also with management of non-radioactive issues.
- For successful and sustainable NORM residue management strategy, the involvement of the stakeholders in the study, and the enhanced communication are fundamental.
- Societal challenges are expected related to the (re)use and/or recycle NORM residues.

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