Application for a Raw Materials Commitment

Innovative, Zero-waste Production of Phosphoric Acid using Hydrochloric Acid and Wastes Valorisation

Acronym:
InPhosphoChlor

Abstract / executive summary:
The production of phosphate fertilizers is needed to improve yields to feed a growing world population. The bulk of phosphate fertilizers are produced by processing Phosphate Rock (PR), which is classified as a Critical Raw Material (CRM). The primary processing approach uses a sulphuric acid leach, which creates Phosphoric Acid (PA) for the fertilizer industry and generates large-volume of PhosphoGypsum (PG) waste, disposed in open-air stacks. This approach has various economic and environmental drawbacks, including the loss of other strategic elements (such as Ni, Cu, Zn, Fe, Al, V, U) and/or CRMs such as rare earth elements (REEs), Sb and Cr, that can occur in appreciable amounts in the PR, and the transfer of harmful elements such as radioactive species, cadmium, arsenic to the environment.
The objective of the commitment is to study the entire PR process chain to both improve yield/range of recoverable commodities and to reduce environmental impact. This will be accomplished by advancing the Technology Readiness Levels (TRL) of hydrometallurgical processes for both PR and PG, thereby offering a new PR alternative and an option for cleaning up and valorising the PG wastes.
Within the SIP-EIP priority actions, the InPhosphoChlor aims at facing European challenges along the processing and refining activities within the raw material value chain.
The philosophy is to achieve near zero-waste and to valorise products and by-products to make the process economically feasible and sustainable. New metallurgical flow sheets will be integrated by new beneficiation, electrochemical, and bio-hydrometallurgical routes to: improve the efficiency of the complete process, increase the range and yields of recovered commodities (e.i. REEs), purify and promote the bulk by-products (calcium chloride and pure gypsum), increase flexibility in terms of types of feed stocks, decrease the environmental footprint of the industry by a zero-waste approach, and advance them to the TRL6.

Links to the Strategic Implementation Plan:
- Technology Pillar
  - I.B Priority Area: Technologies for primary and secondary raw materials’ production
    - Action area n° 1.4: Processing and refining of raw materials
1) Innovative and flexible processing
2) Metallurgical systems

Coverage of the Action Areas referred to above:

Within the Strategic Implementation Plan (SIP) - European Innovation Partnership (EIP) priority actions, the InPhosphoChlor commitment aims at facing European challenges along the processing and refining activities within the raw material value chain.

In particular, the commitment is linked with the SIP-EIP on Raw Materials (RMs) in the framework of the action 1 (Innovative and flexible processing) and 2 (Metallurgical systems) of the Action area I.4 “Processing and refining of raw materials”, under Priority Area I.B “Technologies for primary and secondary raw materials production” of the Technology Pillar.

How InPhosphoChlor addresses SIP-EIP priority actions:

1) the proposed methods will greatly increase the range of recovered CRMs (REEs, Sb, Cr), U, and other metals (e.i. Ni, Cu, Zn, Fe, Al and toxic metals such as Cd, As) from complex and low-grade PRs. The zero-waste approach will promote all products and by-products, will reduce the environmental footprint and will facilitate public acceptance, by the application of innovative, integrated and flexible processing and metallurgical systems;

2) the programme of activity will advance the TRLs of two new metallurgical systems, both linked to the process chain of phosphate fertilizers and the recovery of CRMs (phosphate rock, REEs, etc.): a) hydrochloric acid processing of PR; and b) re-mining and processing of PG. Both metallurgical systems are finalised to recover major and trace products and by-products (high purity PA, REEs, strategic elements, toxic metals, gypsum, calcium chloride, sodium fluorosilicate, etc.) at high grade of purity, and to create economically feasible processes that are near zero-waste.

Objectives of the commitment:

1) Develop innovative PR processing route, which allows for the recovery of associated trace elements at high degree of purity, production of high-purity phosphoric acid, and valorization of waste by-products;

2) develop innovative PG waste treatment techniques that yield safe, marketable gypsum and recovery of value-added trace elements at high degree of purity. The studied methods will be advanced from TRL3 to TRL6;

3) achieve objectives and targets of the EIP on RMs by:
   - innovative, integrated and flexible processing and bio-hydrometallurgical systems to recover “neglected” resource (i.e. REEs);
   - sustainable supply of CRMs to the European economy, thereby improving supply conditions and diversifying sources;
   - technological advancement that will move Europe to the forefront in mineral processing;
   - reducing environmental and health impacts by zero-waste approach.

Description of the activities:

The central themes of the activity aim the development of new integrated metallurgical methods for PR and PG processing that recover additional CRMs, valorizes all products and by-products, towards zero-waste production. The scale-up of the processes will be realized at pilot scale, to illustrate the commercial potential of the developed approaches. Activities, technical methodologies and approaches have been divided in six steps:

Step 1
Chemical-mineralogical characterization of PR and PG samples collected from the various study sites, and sample collection for the metallurgical test to be conducted in the following steps.
Step 2
PR processing
The proposed method produces high purity PA, no waste and provide an added value for the recovery of other CRMs. The flow-sheet will illustrate a general structure demonstrated at the laboratory scale (TRL3); activities will integrate new steps and scale up the process to the small pilot level (TRL5), involving new techniques for magnetic separation, new hydrometallurgical processes, and the use of new techniques for the recovery of high purity metals. These may include metals (e.g., Ni, Cu, Zn, Fe, Al, Sb, V and toxic metals, e.g., Cd, As, and Cr) thus preventing their accumulation in the final PA-based fertilizer.

Step 3
PG processing
The proposed method aims to eliminate the environmental hazard of PG waste by extracting polluting radioactive elements (e.g., U), toxic metals (e.g., Cd), and strategically valuable CRMs (e.g., REEs), with the final goal of near zero-waste. The final product is a purified gypsum or calcite (which can be marketed for numerous building or construction purposes) and the mentioned accessory elements; both products will add high value to the process chain and make it economically viable. Work in InPhosphoChlor will integrate an innovative purification step and will scale up the process to the small pilot level (TRL5). This step will not only provide a purer and easily marketable end by-product (e.g., gypsum) but will also recover useful metals (e.g., Ni, Cu, Zn, Sb, Mn, Fe, V) and toxic metals that could harm the environment (e.g., Cd, Cr, As).

Step 4
Piloting
1) PR
Beneficiation pilot plant already existing will be utilized to meet the objectives. The plant has the potential to conduct various mineral processing operations such as crushing, grinding, gravity concentration, high and low intensity magnetic separations and froth flotation, and also involves a high standard process automatic control system. The concentrates produced by the previous pilot plant will be submitted to hydrochloric acid leaching pilot testing based on the flow sheet and parameters optimised in the step 2. The overall recovery of phosphorus oxide, as well as the trace valuable elements such as REEs, U and Th, will be improved. Results will feed into the LCA and economic feasibility studies in the subsequent step 5.

2) PG
Hydrometallurgical pilot plant will be built for the PG testing. The pilot will be sufficiently flexible to allow for incorporation of any design developments, due to its modular design and programmable control. The parameters tested in step 3, will be studied in a continuous run. The overall recoveries of purified gypsum, as well as of trace valuable elements such as REEs, U and Th, will be improved. Results will feed into the LCA and economic feasibility studies in the successive step 5.

Step 5
Environmental monitoring, LCA, market studies, by-product characterization, social impact.

Step 6
TRL will be advanced to TRL6.

**Description of the expected impacts:**

1) Advance the EU to the forefront in the area of sustainable exploration, and mining and processing technologies and solutions by developing and applying innovative, efficient, economically and environmentally sustainable processes, easy to adopt by EU companies;
2) improve competitiveness and targeting creation of added value and new jobs in materials producing and downstream industries by developing new methods that will provide a valuable EU source of REEs for downstream industries, by further advancing EU industries adopting the new processes;
3) unlock a substantial volume of various raw materials within the EU enabling the better efficiency of exploitation of raw materials’ resources and increasing the range and yields of recovered raw materials. Industrial implementation of proposed methodology will recover large quantity of REEs, U and valuable elements in the EU;
4) enable the better efficiency of exploitation of raw materials’ resources; the proposed additional extraction of trace REEs/CRMs would thus increase the efficiency of the process, as these strategic elements would not be lost but rather CRMs would be recovered without additional up-stream costs;
5) improve economic viability and investment security. The proposed linking of the process chain with other high-value commodities including REEs, as well as bulk commodities, will result in greater economic viability and long-term stability;
6) increase process efficiency and reduce environmental footprint. The proposed PR method will not emit any gypsum, REEs, heavy metals or radioactive elements, aiming for zero-waste. Reduction of cooling water consumption, process water and electricity consumption are also foreseen. Valorisation of PG waste will also greatly reduce the environmental footprint.

**Expected innovation outcomes:**
New products to the market
New processes
New technologies
Societal innovation

**Comments:**
The production of phosphate fertilizers is needed to improve yields to feed a growing world population. The bulk of phosphate fertilizers are produced by processing PR, which is classified as CRM.
At present, the production of phosphorous mineral fertilizer results in large volumes of un-useable waste, as well as the transfer of trace and/or toxic elements from the original PR to both the final marketable PA and waste PG products. This results not only in a significant environmental footprint for the entire process chain, but also the loss of valuable secondary elements, compounds, and materials (including some CRMs and strategic elements). To date, these trace and toxic elements are typically not removed due the very high additional costs incurred by modifying the presently used industry standard technique.

**Name of the coordinating organisation:**
Consiglio Nazionale delle Ricerche (CNR)

**Country:**
Italy

**Entity profile:**
Governmental/public body

**Role within the commitment:**
Coordination and Management. The operating unit of the CNR within the proposed activity will be the "Institute of Environmental Geology and Geoengineering" (IEGG). Its main role will be the extraction and purification of CRMs such as REEs and valuable metals at high-degree of purity, applying innovative processes, especially those electrowinning.
Other partners:

Name of partner: ARMINES (Association pour la Recherche et le Développement des Méthodes et Processus Industriels)
Country: France
Entity profile: Other
Other: Private non-profit organisation
Role within the commitment: Research Partner for analytical characterization (chemical, mineralogical and textural analyses), chemical engineering (clathrate crystallization etc.) and hydrometallurgy (leaching, precipitation, solvent extraction etc.). The operating unit of ARMINES within the proposed activity will be the SPIN (Sciences des Processus Industriels et Naturels) centre, common research centre of ARMINES and "École Nationale Supérieure des Mines de Saint-Etienne".

Name of partner: The Research Committee of the Technical University of Crete (TUC)
Country: Greece
Entity profile: Academia
Role within the commitment: Research Partner for mineral processing, hydrometallurgy, waste valorization and Life Cycle Analysis (LCA). The operating unit of the TUC within the proposed activity will be the School Mineral Resources Eng. including the laboratories of Ore beneficiation, Waste Management and Ceramics Technology.

Name of partner: Universitatea Babes Bolyai (UBB)
Country: Romania
Entity profile: Academia
Role within the commitment: Research Partner for environmental impact. The operating unit of the UBB within the proposed activity will be the Faculty of Environmental Science and Engineering.

Name of partner: Università degli Studi di Roma La Sapienza (DICEA)
Country: Italy
Entity profile: Academia
**Role within the commitment:**
Research Partner for by-product valorisation, materials testing, marketing.

**Name of partner:**
Geologian Tutkimuskeskus (GTK)
**Country:**
Finland
**Entity profile:**
Governmental/public body
**Role within the commitment:**
Research Partner for physical mineral processing (magnetic separation) and piloting. The operating unit of the GTK within the proposed activity will be the GTK Mineral Processing.

**Name of partner:**
State Higher Educational Institution "National Mining University" (NMU)
**Country:**
Ukraine
**Entity profile:**
Academia
**Role within the commitment:**
Research Partner for solvent extraction - Solid Extractants (TVEX), Life Cycle Analysis (LCA). The operating unit of the (NMU) within the proposed activity, will be the Mining Institute, International Projects Department.

**Name of partner:**
Ustav Geotechniky Slovenskej Akademie Vied (UGT-SAV)
**Country:**
Slovakia
**Entity profile:**
Governmental/public body
**Role within the commitment:**
Research Partner for bio-metallurgy (bio-precipitation).

**Name of partner:**
Private Joint Stock Company "Dniprovskiy Plant of Chemical Fertilizers" (PJSC DMZ)
**Country:**
Ukraine
**Entity profile:**
Private sector - large company
**Role within the commitment:**
Industrial partner. End-user. The main role will be testing the innovative processes at industrial scale. Chemical analysis.
Name of partner: Office Chérifien des Phosphates (R&D OCP)
Country: Morocco
Entity profile: Private sector - large company
Role within the commitment: Industrial partner. End-user. OCP is a world leader in the production chain of phosphates. OCP's mission is innovation in the phosphates, with particular reference to the development of new technologies and new products in the ore-processing chain (search-development extraction). Its main role will be testing the innovative processes at industrial scale.

Existing EU contribution: No

Period to implement the commitment: Friday, 1 April, 2016 to Thursday, 31 December, 2020