Putting all the cards on the table

Fertilizers Europe hosted a *Decadmiation Workshop* in Brussels on 2 October 2013 that attracted over 70 participants from knowledge institutes, the European Commission, national authorities as well as the fertilizer industry who debated and discussed all facets relating to the issue of setting cadmium limits in the phosphate fertilizers sold in European markets. The meeting comprised a total of three sessions and a concluding panel discussion, with the purpose of promoting a better understanding between all the interested parties and to seek solutions to a particularly complex problem.

Cadmium (Cd) is a trace element that occurs naturally in soils but has no known functions for the plant. It is readily absorbed by plant roots and translocated to above-ground parts. Although the Cd concentration in soils represents only a small fraction of the total soil exchangeable cations, Cd can affect the ecosystem due to its pronounced toxicity even at trace levels. (*Revisiting and Updating the Effect of Phosphorus Fertilisers on Cadmium Accumulation in European Agricultural Soils*, Prof. Erik Smolders, University of Leuven. Paper presented to International Fertiliser Society [May 2013] (IFS Proceedings No. 724).)

The World Health Organisation (WHO) defined the tolerable daily dietary Cd intake to be 58 µg Cd/day. The European Food Safety Authority (EFSA) has set the limits even lower for Europe, stating a tolerable weekly intake of 25 µg Cd/day. This is close to the upper limit of Cd found in soils and emphasises the importance of avoiding excessive accumulation of Cd in soils through additional inputs.

Cd occurs naturally as an impurity in phosphate rock at concentrations of 1-200 mg Cd/kg P_2O_5 and is present in commercial phosphate fertilizers. The application of P fertilizers is seen as the main source of annual addition to Cd in the agricultural soils of Europe.

Several actions have been taken worldwide to reduce Cd inputs to soils. As a result of technological advances and the enforcement of emissions controls, atmospheric depositions of Cd have decreased. The European Commission is meanwhile contemplating a draft proposal to set limits for Cd content in phosphate fertilizers. This proposal is currently the subject of considerable debate within the European Union (EU) and was the principal reason why Fertilizers Europe convened the Decadmiation Workshop.

The draft proposal on Cd limitation within the EU was based on a risk assessment in 2002 by the European Scientific Committee, Ecotoxicity and Environment (CSTEE). A mass balance approach was used, with the goal of setting limits on Cd in fertilizers such that annual application would not lead to the long-term accumulation of Cd in European agricultural soils. Values were thus calculated for which the net annual input of Cd in soils equals the net annual output of Cd through leaching or removal by crops. This 2002 study demonstrated that when P fertilizers containing a maximum 20 mg Cd/kg P_2O_5 are applied to the fields, no net increase in soil Cd was expected in most scenarios.

Industry alarm

Many European fertilizer suppliers view the prospect of an EU limit on Cd content in line with this 20 mg Cd/kg P_2O_5 criterion as draconian and impracticable. Green political parties and other environmental could be expected to welcome it, however. Between these poles of opinions, the Fertilizers Europe decadmiation workshop provided a forum where all interested parties could discuss and debate every facet of the issue. The following topics were addressed:

- Cadmium limits in fertilizers under today's as well as future fertilizer regulation
- Current science on Cd removal technologies
- Available Cd removal technologies
- Potential use of cadmium isolated from phosphate rock or phosphoric acid.

In his welcome to participants, **Jacob Hansen**, Fertilizers Europe Director General, said that debate and discussion would provide a better understanding of the issues and point the way towards finding solutions. Fertilizers Europe seeks to retain a viable European fertilizer industry while ensuring effective environmental protection. Mineral fertilizers are essential to life and feed 50% of the world's population. Phosphate fertilizers make a major contribution to providing enhanced global food security. Originating from natural ores which do contain some impurities, including cadmium, impurities are also found in phosphate fertilizers.

Several Cd removal (decadmiation) technologies exist, but none cover all fertilizers and none are at present used in an industrial scale for fertilizer production. Jacob Hansen summed up the objectives of the workshop as:

- To bring together technology providers, companies active in phosphate fertilizer production or the agricultural sector,

knowledge institutes and regulators (at both European and national levels).
- Provide information on the state of the art in Cd reduction technologies and provide a platform for phosphate fertilizer producers to demonstrate their developments in this area.
- Give an update of the current and future Cd balance in European agricultural soils.

Jacob Hansen acknowledged the challenge of finding suitable Cd limits while maintaining an effective European fertilizer industry, but an important first step will be to establish an agreed scientific basis for any such limits and to explore avenues for an equitable solution.

Defining the issues

Vincent Delvaux, DG Enterprise of the European Commission opened the discussion by asking, *Cadmium in phosphate fertilizers: is this an issue?* He said that the Commission is working on a revision of the existing Fertilizer Regulation. Limiting Cd content in phosphate fertilizers is being considered in this context.

Delvaux reviewed the scientific data that has been gathered to date, as well as outlining the current regulatory framework and options for future regulations. He noted that P fertilizers contain Cd as a natural impurity in amounts that depend on the source of the phosphate rock from which they are produced. Cd tends to accumulate in the environment and, depending on soil and climate conditions, some Cd is taken up by the plants and subsequently ingested by humans via the food chain. Cd is toxic to humans and can accumulate to levels that adversely affect kidney function.

Fertilizers are an important contributor to the presence of Cd in the food chain, but the incidence of Cd pollution is not uniform in Europe. In 2012, after the Swedish government notified the European Commission of its intention to reduce its national provision of the Cd content in phosphate fertilizers from 100 mg Cd/kg P_2O_5 to 46 mg Cd/kg P_2O_5, SCHER (EU Scientific Committee on Health and Environmental Risks) provided an assessment of the overall scientific quality of the Swedish report, commenting on the proposed scenario and evaluating the assumptions made. These were found not to be valid overall, but SCHER noted that the CSTEE opinion of 2002 was based on a stand-still principle, and not on a risk assessment basis.

Fertilizers, manure, lime, sludge and tobacco are the only sources of Cd that have not been addressed via risk mitigations at EU level so far. Vincent Delvaux noted that action by EU member states is limited because most inorganic fertilizers traded in Europe are EC fertilizers which do not have to comply with limits on Cd. The use of the mutual recognition of national fertilizers is another issue which cannot be solved by individual action from member states.

Delvaux commented that it is difficult to determine a suitable risk-based Cd limit. The EC Risk Reduction Strategy for Cadmium (2008) recommended that concrete measures be taken to reduce Cd content in food, tobacco and fertilizers. EC Regulation No. 2003/2003 covers inorganic fertilizers but set no maximum Cd limit. Derogation was granted to Sweden, Finland and Austria to maintain their national Cd limits. Two options for regulation are being considered. One is to continue with the status quo, but with diverging limits across the member states, ranging between 20-90 mg Cd/kg P_2O_5. The other option is to set an EU limit for all EC and national inorganic phosphate fertilizers, with the goals of reducing Cd inputs into the environment and simplifying the regulatory framework.

How should the problem of Cd in fertilizers be addressed? Delvaux suggested that account should be taken of the variety of climate and soil conditions within Europe, as well as the need to simplify the regulatory framework. There should also be incentives for industry to invest in decadmiation technologies.

Prof. Erik Smolders of the Catholic University of Leuven discussed *Cadmium in soils: from accumulation to depletion*. Prof. Smolders explained that current approaches are based on "zero accumulation studies", as per the CSTEE assessment of 2002, rather than risk assessment studies. The CSTEE assessment essentially searched for a Cd content in P fertilizers that would not lead to a significant increase in soil Cd concentration over time, for example 100 years. He presented an update of this 2002 study. The same soil mass balance (i.e. Cd inputs less Cd outputs) was used, but the parameters were revised. This update was warranted because:

- There has been a drastic decrease in atmospheric deposition of Cd as the result of reduced emissions as well as better monitoring and measurement equipment
- Phosphate fertilizer use has decreased
- There is now a better knowledge on the leaching of Cd from the topsoil.

The results of this study showed that on average, using a P fertilizer containing up to 80 mg Cd/kg P_2O_5 will not result in a Cd accumulation in agricultural soils over time (100 years).

Prof. Smolders noted that within the EU, there is evidence of Cd reduction or steady state, possibly due to reduced P_2O_5 fertilizer consumption and lower atmospheric depositions. He also commented that EU soils are more acid than previously estimated and thus leach metals more easily. Studies at the Rothamsted research centre in the UK have shown that Cd content in topsoil was rising up to around 1984, at the rate of 2.5 g Cd/ha/year, of which around 2 g Cd/ha was attributable to P fertilizer applications. Total Cd soil content was estimated at around 900 g Cd/ha in a 1987 study.

Against the background of proposed regulation based on a steady-state principle of zero Cd net accumulation, Prof. Smolders commented that modelling rather than monitoring would provide a better basis of driving the stand-still system. He concluded that the current average EU Cd mass balance is now negative compared with the positive balances estimated in 2002 and earlier.

Rannveig Anna Guichernaud spoke on *Topsoil cadmium concentration in European soils in relation to land use*, outlining the preliminary results from the LUCAS (Land Use/Land Cover Area Frame Survey) topsoil survey, with the goal of gaining knowledge of the distribution of heavy metals in soils and their link to land use systems. This survey represents the first attempt to build a consistent spatial database of the soil cover across the EU, involving around 20,000 samples that were collected and analysed. In 2011, it was decided to add analyses of heavy metals to the survey, including Cd and Zn. Currently 5,800 samples have been analysed.

In general, Cd and Zn levels were below soil guideline values. On average, higher Cd and Zn values were found in forest and wetland areas compared with cropland and grassland. This appeared due to the higher affinity of Cd and Zn to organic matter, although no linear relationship. No statistical difference was found between land use classes in Cd and Zn concentrations due to the high variability between each land use class. No clear relationship was found between Cd and other possible factors, such as pH, Fe or P. However for Zn, a positive correlation was found in cropland and grassland for Fe and P. These cover classes frequently receive P fertilizer inputs, thus explaining the P/Zn relationship.

Antoine Hoxha, Technical Director of Fertilizers Europe, provided an overview of decadmiation technology and listed the Cd limits introduced outside the EU. Some of them are based on risk assessment and range from 122 mg Cd/kg P_2O_5 in New Zealand to a maximum of 400 mg/kg P_2O_5 in Australia.

There is a very limited availability of low-cadmium phosphate rock, so fertilizer producers must opt for removing the Cd during downstream processing. Several Cd removal technology routes are available:

- Phosphate rock calcination. This is done at 1000ºC in a neutral or reducing atmosphere.
- Decadmiation of phosphoric acid. Several technologies are available (co-crystallisation, sulphide precipitation, ion exchange, solvent extraction and membrane technologies).

Criteria for evaluating the merits of these various technologies include technological feasibility, achievable Cd abatement, costs, whether any waste is generated and other impacts. All available technological options should be re-evaluated, Antoine Hoxha concluded.

Dr. Carsten Gellermann of Fraunhofer ISC discussed *Separation technologies and applications of cadmium.* Among the industrial applications for cadmium are as a stabiliser in PVC, in pigments and coatings and in nickel-cadmium batteries. Global production of industrial Cd is estimated at 20,000 t/a. Cadmium markets are not growing overall, especially following the wider use of nickel batteries.

Two feasible decadmiation technologies in zinc production are based on hydrometallurgical processes (calcination to zinc oxide) and pyrometallurgical processes.

Sedimentary phosphate rock has cadmium concentrations ranging between 20-200 mg Cd/kg P_2O_5. Calcinating phosphate rock (via the addition of chlorides, or in an oxidised or neutral atmosphere) is relatively costly, incurring costs of around \$30/t P_2O_5. Co-crystallisation is a much cheaper option. The process is very good with nickel cadmium batteries, which account for most of global Cd consumption.

While the Cd removed from phosphate fertilizer production processes could be valorised, this would only represent a fraction of the total Cd use. Also the cost of treating Cd-rich waste is often overlooked when calculating the costs of decadmiation technologies and could be very significant.

Fertilizer producers face several challenges in their efforts to limit Cd content: a reduction in Cd content is the preferred medium- and long-term option. Dr. Gellermann concluded that further investments are needed to optimise the existing technologies, and further evaluation is necessary to improve cost-effectiveness.

Assessing Cd removal technologies

Marc Collin, Managing Director of Prayon Technologies s.a. and in charge of the Prayon's Profile Equipment Division, described *Limiting cadmium content in phosphoric acid*. The presentation is based on a previous review performed in the early 1990s. There are four basic processes:

- Cd co-crystallisation in anhydrite (CC)
- Cd precipitation in sulphur compounds (PP)
- Ion exchange (RX)
- Solvent extraction (SX).

OTP, Togo in conjunction with Pierre Becker developed a co-crystallisation process as part of the post-acid treatment phase of MGA by adding sulphuric acid and monocalcium phosphate (MCP). A similar process has been trialled by OCP, Morocco, with each attaining yields of over 90% in tests. Waste comprised less than 1% Cd. The process also removes barium and strontium. The co-crystallisation facility should be located close to the phosphoric acid plant. At 1990s prices, the estimated capital cost for treating capacity of 500 t/d P_2O_5 was in the EUR 3-4 million range, while operating costs at 1990s prices were under \$10/t P_2O_5.

The precipitation process involves the addition of a sulphur-containing reactant to the phosphoric acid, resulting in the formation of Cd-sulphur precipitates which are removed through filtration. Patents have been registered by Siape, OCP and Hoechst. The process yields up to 90% Cd, with wastes of between 1-10% Cd. These wastes should be treated. The process also removes Zn, Cu, arsenic (As), Mo and zirconium (Zr) from the acid. The precipitation plant can be remotely located. Capital expenditure is on a par with the co-crystallisation process but operating costs are double due to the cost of reactants.

Several ion exchange processes have been studied. The merchant-grade acid should be pre-treated before the Cd is extracted by means of cationic or anionic resins. Yields of between 85-95% can be achieved, with Mg, Ca and Fe also removed. The ion exchange facility should be adequately located close to the phosphoric acid plant. Capital cost of the facility for a treating capacity of 500 t/d P_2O_5 is estimated at EUR 5-10 million in 1990s prices, while operating costs are estimated at between EUR 25-30/t P_2O_5.

Solvent extraction (SX) also involves the pre-treatment of the acid, producing Cd as a 15-20% Cd basic solid. The process was patented by Budenheim and also achieves a yield of over 90% with removal of Mo, Zn, Cu and Mg. Capital expenditure for treating a capacity of 500 t/d P_2O_5 is high and operating costs are estimated at over EUR 30/t P_2O_5.

Assessing the merits of the various acid treatment processes, Marc Collin regarded CC as best for integration with phosphoric acid production and it is also the cheapest. PP is applicable to merchant grade acid production but its suitability is dependent on the costs of the reactant used. The RX and SX processes require pre-treatment of the MGA, resulting in the production of a high-grade cleaned acid. Treatment of the waste poses a problem: should they be solid or diluted in liquid? The estimated capital and operating costs, based on 1990s data, need to be actualised.

Marc Collin described Prayon's recent work in the decadmiation field, outlining the recently-developed dihydrate-hemihydrate (DA-HF) process. This process has the goals of improving the dihydrate (DH) P_2O_5 recovery process along with lower steam consumption. Industrial tests have been performed in partnership with Grupa Azoty of Poland. During the tests, it was observed that the DA-HF process may offer a lower Cd content in the acid compared with the normal DH process. Prayon Technologies also conducted R&D works, resulting in a patent taken in 2008 with OCP Cerphos for the treatment of Cd-containing solids produced by a CC process.

The principal objective was to develop a quick treatment process with an easy recovery of Cd and production of high Cd concentrates. Cd precipitation with sulphides produces a 32% CdS concentrate for further use or disposal.

Ole Bjørn Jenssen¸ Yara's head of technology and mining operations, discussed *Yara's experiences with decadmiation*. Yara has no Cd removal facilities at its existing phosphoric acid and NPK plants, as they were designed to process low-Cd Kola rock. However, Moroccan phosphate rock is being more widely used by Yara and has a higher Cd content, thus compelling Yara to prioritise the development and installation of Cd removal technologies.

Yara's acquisition of Kemira GrowHow enabled the low-Cd NPK production facilities to be relocated from Glomfjord in Norway to Uusikaupunki in Finland. In Yara's experience, the type of phosphate rock being used mainly determines the distribution between calcium sulphate and phosphoric acid, rather than the acid production process. In Yara's NPK plants in Norway, all the Cd from the phosphate rock ended up in the NPK fertilizer: none followed into the calcium nitrate by-product.

Yara began work on research and testing of decadmiation technologies in 1979. The main focus has been on the nitrophosphate (NP) process used in Norway. To date, the company has tested the selective leaching phosphate rock, as well as calcination, precipitation, ion exchange and the use of substitute sources of phosphate rock. A trial of membrane technology proved unsuccessful.

Yara has been able to achieve reductions in Cd content, but the company has not yet found a solution that isolates and removes cadmium from the NP process in a technically feasible way. The cost of incorporating chemicals in decadmiation processes is estimated to add over \$100/t to total production costs and is clearly uneconomic.

Yara's most recent work has focused on reducing cadmium levels in phosphoric acid produced by the hemihydrate process via precipitation. Tests have shown that Cd precipitated and allocated to the by-product phosphogypsum in the phosphoric acid production process is feasible, but the cost is very high, at over \$50/t P_2O_5.

One challenge in the NP process is that the excess hydrochloric acid produced after the digestion of the phosphate rock creates problems with the stability of different agents which could normally be used to reduce Cd content. Other practical problems included clogging and the need to use bigger filters. Precipitation in theory is feasible, but the process incurs large P_2O_5 losses, of up to 30%.

In all, while much research and development work has been undertaken, Yara has to date been unable to isolate and upgrade the cadmium in a technically feasible way. A potentially more promising route is offered if Yara decides to proceed with one of two goldfield mining projects in Finland and Canada, which also promise the production of phosphate rock with a cadmium content of below 5 mg Cd/kg P_2O_5.

Yara continues to work on decadmiation technology as it is not comfortable with being dependent on purchasing phosphate rock for its Norwegian plants.

Ludwig Hermann, senior consultant for energy with Outotec, discussed the *Potential of thermal processes for cadmium removal*. He outlined the ASH DEC calcination process, whereby it is possible to remove impurities and pollutants at temperatures of 850-1,000ºC. Lab and pilot experiments have shown an effective removal of Cd of around 80%. For example, rock which contained 44.70 mg Cd/kg P_2O_5 pre-treatment showed cadmium levels of 2.52 mg Cd/kg P_2O_5 post-treatment. Residual levels of less than 0.1 wt% organic and inorganic carbon were also demonstrated. The Outotec thermal process enabled the oxidisation of solid cadmium oxides while the carbonates were destroyed. This resulted in gaseous elementary Cd, which can easily be evaporated at higher temperatures.

The process requires further testing. Whilst 100% efficiency calcination cannot be achieved, similar technology that is currently used in the aluminium industry could be transferred to the phosphate industry. Up to 2,000 t/d of phosphate rock could be processed in this way. Once calcined in this process, the phosphate rock is less reactive. The cadmium condensates and accumulates as a dust. Other products are also present as dust, including 2-3% P_2O_5: the loss of P_2O_5 efficiency is unavoidable. Energy costs with the thermal process are high, being estimated at around EUR 40-80/t.

Lively panel discussions

Under the very skilled stewardship of **Sonja van Renssen** as moderator, the formal presentations were followed by a panel discussion and debate. This proved timely, as on 8 July 2013, the DG Environment officially launched the public consultation on sustainable phosphorus use. The consultation period was due to end on 1 December 2013.

The issue of the sustainable use of fertilizers in agriculture is also under consideration, as well as product safety and use: EU member states may have the flexibility to bring in their own regulations. A participant from the UK said that DEFRA (Department for Environment, Food and Rural Affairs) favours a risk-based approach, rather than the hazard-based approaches so far mooted. There is no current UK regulation, other than for Cd content in sewage. The UK delegate advised that any regulations and restrictions should be proportionate and avoid loading additional costs on to producers and consumers without ignoring the environment protection issues. He also urged a policy of "horses for courses": regulations that may be acceptable for Nordic countries may not be appropriate for Southern European member states.

Another delegate enquired about the greenhouse gas (GHG) implications of the calcination route to Cd removal. Would Cd regulation for fertilizers be worth the impact of processing on GHGs? The impact on the competitiveness of the EU food processing sector should also be assessed. The disposal of the Cd removed likewise poses problems: up to 2,000 t/a Cd from zinc processing is disposed as landfill. What tonnages would result from phosphate decadmiation?

The discussion panel noted that decadmiation processing technology requires further development and its economic viability needs to be proven. **Eberhard Gschwindt** from the European Investment Bank indicated that EIB could finance R&D activities before the regulatory framework is finally set, as well as industrial-scale projects once the timeline of such regulatory framework is set.

Antoine Hoxha concluded the workshop with a summary of the key points raised. He noted the great diversity of opinions that were very illuminating. He believed that there is now the basis for a shared knowledge and a better basis for discussion and reaching decisions. Prof. Smolders has provided a landmark paper, which has still to be peer-reviewed. Some of the technological routes show greater promise than others, much more R&D and pilot work is required as none is yet ready for industrial-scale use. Does the EU truly need such low Cd limits as 20 mg Cd/kg P_2O_5? Whatever the ultimate decision reached on Cd limitation and regulation, risk assessment provides a better basis than hazard assessments. Nor should we lose sight of the use of fertilizers in the provision of food, Antoine Hoxha concluded ■