

PROGRESS IN THE DEVELOPMENT OF DECADMIATION OF PHOSPHORUS FERTILIZERS

J. Keith Syers

*Professor of Natural Resources, Faculty of Agriculture, Natural Resources, and
Environmental Sciences, Naresuan University, Phitsanulok 65000, Thailand*

Abstract

Interest in decadmiation of phosphate rock (PR) and phosphoric acid reflects concerns regarding the possible harmful effects of cadmium on ecosystem and human health.

Calcination is essentially the only effective method for removing cadmium from PR. Heating to 850-1150⁰C decreases the cadmium content substantially, for example with Nauru PR from about 600 to less than 120 mg kg⁻¹ P, but the cost involved is substantial. There appears to be no current interest in calcination for cadmium removal.

There are several methods for removing cadmium from wet-process phosphoric acid. These include:

- Co-crystallisation with anhydrite
- Precipitation with sulfide ions
- Removal by solvent extraction
- Removal by ion exchange
- Separation by membrane technology

Of these, anhydrite co-crystallisation appears to be the most promising, although very recently there has been interest in membrane technology separation. Estimates of costs of cadmium removal vary but are thought to be between US\$20 and US\$45 tonne⁻¹ P at the primary production stage.

Because of the cost involved in decadmiation and the present uncertainties of risk from cadmium, decadmiation does not appear to be a priority issue for the fertilizer industry, particularly in Australia. This situation could change, however, especially in Europe where consideration is being given to introducing maximum cadmium levels which are appreciably lower than those used at present. If implemented, this will increase the cost of low-cadmium containing PRs, with implications for the fertilizer industry in many countries, including Australia.

Background

There is increasing concern regarding the likely impact of cadmium in the environment. This arises because cadmium is a toxic and carcinogenic element, which poses risks to ecosystems and humans, and is hazardous in excessive amounts (SCOPE, 2000). Cadmium has been linked to bone disease in Japan and more widely to kidney disfunction in environmentally-exposed populations, but cancer is not currently regarded as a risk from cadmium ingestion at levels encountered in the environment. There are uncertainties regarding the medical issues but the precautionary principle dictates that, in the absence of appropriate data or in the presence of uncertainty, risks be managed at low levels, until data are available to indicate that less protection is required or acceptable (SCOPE, 2001).

Food is the major source of environmental cadmium for humans and the main inputs of cadmium to the food chain are from additions to soil (McLaughlin and Hamon, 2001). Inputs of cadmium to agricultural soils occur by atmospheric deposition and by additions of sewage sludge (biosolids), animal manure, and phosphorus fertilizers. The view is emerging in certain quarters that cadmium from phosphorus fertilizers poses a potentially serious threat to soil quality and, through the food chain, to human health (Oosterhuis *et al.*, 2000).

Interest in reducing cadmium inputs to the environment, and particularly into the food chain, from phosphorus fertilizers have focussed attention on the possibility of removing cadmium from PR and the phosphoric acid used to manufacture high-analysis, phosphorus-containing fertilizers—a process usually referred to as decadmiation.

The cadmium content of PR materials varies appreciably and ranges from about 1 to more than 600 mg kg⁻¹ P (Table 1). Igneous deposits have lower cadmium contents than sedimentary deposits but account for only 5 per cent of world reserves and 13 per cent of present world production (Van Kauwenburgh, 1997). This very wide range in cadmium content means that the potential requirement for decadmiation varies appreciably, assuming that the need and commercially viable industrial processes exist.

Table 1. Cadmium and phosphorus contents of the main commercial phosphate rocks (taken from McLaughlin and Hamon, 2001)

Phosphate rock (P)	Cd (mg kg ⁻¹)	P (%)	Cd (mg Cd kg ⁻¹)
<i>Igneous</i>			
Kola (USSR)	0.2	17.2	1
Phalaborwa (South Africa)	4	17.2	23
<i>Sedimentary</i>			
Jordan	6	14.8	27
Duchess (Australia)	7	13.9	50 ¹
Arad (Israel)	12	14.1	85
Gafsa (Tunisia)	38	13.4	108
Florida (68% BPL)	16	13.6	115
Bu-Cra (Morocco)	38	15.7	240
Christmas Island	43	15.3	275
North Carolina	47	15.1	311
Togo	51	16.0	320
Taiba (Senegal)	90	15.8	570
Nauru	100	15.6	640

¹WMC Fertilizers quote a value of 20 mg Cd kg⁻¹ P.

This paper briefly reviews recent developments in and the current state of decadmiation technology in the production of phosphorus fertilizers, and concludes with some comments on the Australian situation

Processes for Decadmiation

There are two approaches to the decadmiation of phosphorus fertilizer materials:

- Reduction of the cadmium content of PR by calcination;
- Removal of cadmium from phosphoric acid by a range of physico-chemical processes.

These are discussed briefly below.

Calcination of phosphate rock

Calcination is the only known method for effectively removing cadmium from phosphate rock; neither common PR beneficiation techniques nor selective leaching are feasible (Van Kauwenbergh, 2001).

Calcination is most effective at temperatures between 850 and 1150⁰C, either under an inert atmosphere or reducing conditions. The cadmium oxide produced is very volatile but it is also very toxic. Calcination in the presence of chloride salts allows a temperature as low as 700⁰C to be used (Baechle and Wolstein, 1984) but this results in excessive corrosion.

There was a fairly substantial amount of research on calcination in the 1980s and some of this led to patents. The CERPHOS process, developed in Morocco, decreased the cadmium content of Moroccan PR by 75 per cent, when heated in the range of 750 to 950⁰C under controlled pressure to reduce and volatilize the cadmium (Kossir and Chik, 1996); the estimated cost was about US\$10 tonne⁻¹ of phosphate concentrate. It appears that the only calcination facility in the world for removing cadmium was built by Nauru Phosphate Corporation. This plant operated at a capacity of 75 tonnes hour⁻¹, and decreased the cadmium content of Nauru PR from about 600 to less than 120 mg kg⁻¹ P (Van Kauwenbergh, 2001) The plant has now been decommissioned.

The precise costs of calcination by the different methods are not known but are thought to be in the range of US\$10 to 20 tonne⁻¹ PR, although the cost for calcining Nauru PR appears to have been higher, given that in 1992 Nauru PR was selling for about US\$50 tonne⁻¹ whereas the calcined product sold for over US\$90 tonne⁻¹.

To the knowledge of the author, there is currently no economically viable industrial process for reducing the cadmium content of PR to acceptable levels for the manufacture of phosphorus fertilizers. Also, there have been no recent research publications on the removal of cadmium by calcination. Interest has waned because of economic considerations and because other research has indicated that cadmium removal from phosphoric acid is a more cost-effective route (Van Kauwenbergh, 2001).

Removal from phosphoric acid

There are several processes which have been used to remove cadmium from phosphoric acid produced using sulfuric acid. They may be grouped as follows:

- Co-crystallisation with anhydrite
- Precipitation with sulfide ions
- Removal by solvent extraction
- Removal by ion exchange
- Separation by membrane technology

Davister (1992) assessed the various technologies available for cadmium removal from phosphoric acid available at that time and developed potential costs for their implementation. Of the first four named above (separation by membrane technology is discussed separately at the end of this section), co-crystallisation with anhydrite was seen to be the most promising. However, Van Kauwenbergh (2001) has pointed out that in evaluating the costs some caution should be used in applying the value of the cadmium-containing rejects as a way of reducing the costs per tonne of phosphorus for the co-crystallisation process. He emphasises the very variable and decreasing value of cadmium metal between 1995 and 1999, and the cost of disposing of reject material as a hazardous waste.

A laboratory-scale pilot plant using the anhydrite co-crystallisation process was established at CERPHOS (Morocco) in 1994. This involved elimination of cadmium in the feed acid by co-crystallisation into a precipitate of anhydrite (calcium sulfate) and separation of the latter by settling and/or filtration. A product acid with a cadmium concentration of less than 23 mg kg⁻¹ P was

consistently produced from a feed acid with a cadmium concentration of 170 mg kg⁻¹P (Davister, 1996). This has yet to be taken to the semi-industrial pilot plant scale.

Estimates of costs, both investment and operating, of the four processes above for decadmiation of phosphoric acid are given in Table 2. For comparison the costs for the wet process phosphoric acid (WPA) plant itself are also shown.

Table 2. Estimated investment and operating costs (in millions of US\$) for four processes used for the removal of cadmium from wet-process phosphoric acid in a plant with a capacity of approximately 200 tonnes day⁻¹ P located in Western Europe (based on Davister, 1996)

Process	Conditions	Investment Cost	Operating Cost (US \$ per tonne of P)
Co-crystallisation	Without residue treatment	7	14
	With residue treatment	8	14-21
Precipitation		7	69
Solvent extraction	With full acid pre-treatment	9	73
Ion exchange	With medium acid pre-treatment	9	69
Wet process phosphoric acid manufacture		25	69-92

Davister (1996) points out that these costs have only a relative and an indicative value but they do show that even though anhydrite co-crystallisation is the most promising route, the operating costs are still 20 to 30 per cent of the wet process acid operating costs. The operating costs for the other three processes are substantially higher, being 75 to 100 percent of the WPA operating costs, because of the high cost of the reagents (solvents and resins in the case of solvent extraction) and resins (in the case of ion exchange). The higher added value of feed-grade products can bear the substantially higher cost of decadmiated phosphoric acid produced by precipitation with sulfide ions (as in Tunisia) or produced by solvent extraction (as in Germany).

Recent research into cadmium removal from phosphoric acid has concentrated on liquid membrane technologies. These involve emulsion liquid membranes, supported liquid membranes, and membrane-assisted, non-dispersive solvent extraction (Urtiaga *et al.*, 2000). Cyanex 302 (a monothio-phosphinic acid) has been used as the selective mobile carrier because of its ability to extract cadmium and its high stability in acidic media (Almela *et al.*, 1998). Based on the values of mass transfer flux, it appears that non-dispersive solvent extraction is the most effective for cadmium removal from phosphoric acid. Whether these laboratory-based technologies can be carried to a commercial stage is far from clear.

One membrane (but not a liquid membrane)-based system which has been developed and taken to commercial production is the Simplot Phosphoric Acid Purification Process (Anonymous, 1998). This process has the ability to lower the cadmium concentration in a 19.0 per cent P feed acid (obtained from uncalcined Idaho PR, which is very high in cadmium) from 125 mg l⁻¹ to less than 5 mg l⁻¹. The driving force for the development of this high quality phosphoric acid was the production of a fertigation (drip) grade phosphoric acid. Production is around 30,000 tonnes year⁻¹.

Emphasis in this paper has been placed on WPA produced from a sulphuric acid-PR digestion. Studies indicate that it is more difficult to separate cadmium from solutions obtained by digesting PR with nitric acid (Baechle and Wolstein, 1984). According to Van Kauwenbergh (2001), the Superfos ion exchange nitrophosphate process may remove cadmium, but the amounts which can be removed and the costs are not known.

In the final analysis, it will be costs which will ultimately determine the viability of a phosphoric acid decadmiation technology; these are unclear because none appear to have been implemented for the

production of phosphorus fertilizers and few taken to the pilot plant stage. Van Kauwenbergh (2001) has emphasised that an added cost of US\$23 to US\$46 tonne⁻¹ P at the primary production level for cadmium removal could very easily double by the time the fertilizer reaches the farmer.

The Australian Context

Australia is fortunate in having an indigenous PR deposit (the Duchess deposit at Phosphate Hills), which is very low in cadmium (approximately 20 mg Cd kg⁻¹ P). After Kola (Russia) and alongside Phalaborwa (South Africa), this PR is the probably the lowest commercially available cadmium-containing PR in the world (Table 1). This is used to produce WPA with a cadmium concentration of about 2 mg l⁻¹. The DAP (Aussiegold) manufactured by Western Mining Corporation in Queensland has an average cadmium content of 15 mg Cd kg P⁻¹, which is appreciably lower than that (approximately 90 mg Cd kg P⁻¹) in the MAP imported from the USA.

It should be re-emphasised that decadmiation is really only a commercial possibility for high-analysis products based on WPA. At this point in time, given the low cadmium content of Duchess PR, the cadmium content of WPA and thus decadmiation is not an issue in Australia for high-analysis products, such as DAP. In any case, imported TSP has a typical cadmium content of around 100 mg Cd kg⁻¹, which is well below the current maximum compliance level.

The situation for single superphosphate (SSP) is different, where decadmiation is presently not economically feasible. The four Australian SSP manufacturers do not use the low-cadmium containing Duchess PR but use imported PR from a variety of sources, including China (low cadmium), Christmas Island, Florida, Jordan, Morocco (Bu-cra), Nauru, and Israel. These PR materials vary appreciably in their cadmium content, but some are high (Table 1). The current legal limit (maximum) for the cadmium content of SSP in Australia varies from State to State, but is in the process of being harmonized at a level of 300 mg Cd kg P⁻¹ (McLaughlin, this Conference). This figure is being met by the SSP manufacturers by blending. There is also a current voluntary limit of 250 mg Cd kg P⁻¹ in SSP used for horticultural crops, which again is being met by blending.

What may change this situation is the introduction of a tax on high cadmium-containing P fertilizers in the EU (Oosterhuis *et al.*, 2000). There is current speculation (probably to be resolved in mid-May, 2001) that a step-wise, phasing in of a tax on P fertilizers with a cadmium content above 60-40-20 mg Cd kg P₂O₅⁻¹ (above approximately 140, 90, and 45 mg Cd kg P⁻¹), which will be harmonised across the EU, is likely to occur. These values are very much lower than the current maximum compliance levels in Australia, although it is recognised that application rates of SSP are lower in Australia than are those of phosphorus fertilizers in the EU.

It seems highly likely that one immediate impact of such a cadmium tax will be an increase in the cost of low cadmium-containing PR materials. This will change the economics of SSP manufacture and raises the question of the future viability of SSP manufacture.

Acknowledgements

Several people kindly provided information which has been used in this paper; their contributions are gratefully acknowledged. They include:- Marten Walters (J.R. Simplot Co.), Mr Ian Grant (WMC Fertilizers), Dr Steve Kauwenbergh (International Fertilizer Development Center), Mr Douglas McGuffog (Fertilizer Industry Federation of Australia, Inc), and Dr Mike McLaughlin (CSIRO Land and Water).

References

- Almela A, Elizalde M P, and Gomez J M (1998) 'Cadmium (II) extraction from phosphoric media by bis(2,4,4-trimethylpentyl) thiophosphinic acid (Cyanex 302).' *Fluid Phase Equilibria* 145, 301-310.
- Anonymous (1998) <http://www.kemworks.com/services/pap.htm>
- Baechle H-T, and Wolstein F (1984) 'Cadmium compounds in mineral fertilizers.' *Fertilizer Society Proceedings* No. 226, 18p.
- Davister A (1992) 'Inventaire des Etudes et Recherches sur les Procédes d'Elimination du Cadmium dans l'Acide Phosphorique.' Synthesis Report for the EU Commission and IMPHOS, July, 1992, 44p.
- Davister A (1996) 'Studies and research on processes for the elimination of cadmium from phosphoric acid.' In *Fertilizers as a Source of Cadmium*, pp.21-30. OECD Proceedings, OECD, Paris.
- Kossir A, and Chik A (1996) 'Promoting the development and semi-industrial application of a potentially high performing process for cadmium removal from phosphate rock.' In *Fertilizers as a Source of Cadmium*, pp. 41-44. OECD Proceedings, OECD, Paris.
- McLaughlin M J, and Hamon R (2001) 'Perspectives on inputs of cadmium to the food chain.' In *Environmental Cadmium in the Food Chain: Sources, Pathways, and Risks*. J K Syers and M Gochfeld (eds), pp. 60-65. Proceedings of a Workshop held at the Belgian Academy of Sciences, Brussels, 13-16 September, 2000. SCOPE, Paris.
- Oosterhuis F H, Brouwer F M, and Wijnants H J (2000) 'A possible EU wide charge on cadmium in phosphate fertilizers: Economic and environmental implications.' Final Report to the EU Commission. Report Number E-00/02. Institute for Environmental Studies, Vrije Universiteit, Amsterdam, The Netherlands.
- SCOPE (2000) 'Report from the SCOPE Workshop on Environmental Cadmium in the Food Chain: Sources, Pathways, and Risks' <http://www.icsu-scope.org>.
- SCOPE (2001) 'Environmental Cadmium in the Food Chain: Sources, Pathways, and Risks.' J K Syers and M Gochfeld (eds). Proceedings of a Workshop Held at the Belgian Academy of Sciences, Brussels, 13-16 September, 2000. SCOPE, Paris, 204p.
- Urtiaga A M, Alonso A, Ortiz I, Daoud J A , El-Reefy S A , Perez de Ortiz S, and Gallego T (2000) 'Comparison of liquid membrane processes for the removal of cadmium from wet phosphoric acid.' *Journal of Membrane Science* 164, 229-240.
- Van Kauwenbergh S (2001) 'Cadmium and other potential hazards.' *Fertilizer International* No 380, 51-69. January/February, 2001.
- Van Kauwenbergh S (1997) 'Cadmium and other minor elements in world resources of phosphate rock.' *Fertilizer Society Proceedings* No. 400, 40p.