Waste Treatment

Treatment of Cr^{VI}-Containing Mg(OH)$_2$ Nanowaste**

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Nanomaterials can be very effective for adsorbing heavy metals and organic pollutants from waste water,[1] whereupon they are transformed into so-called nanowastes that can be particularly complex in composition, highly stable in size, and difficult to precipitate. Investigations related to the disposal of these hazardous pollutant-adsorbed nanowastes are yet to be reported.

It has been recognized recently that some traditional industrial sludges are actually nanowastes with adsorbed heavy metals or organic pollutants.[2] For example, Chinese chlor-alkali and chlorate plants generate over 800 kilotons of Mg(OH)$_2$-containing nanowastes per year.[3–5] These nanowastes have a high surface-adsorption affinity and sometimes contain tightly bound poisonous heavy metals or have dioxin-like toxicity.[6] The Mg(OH)$_2$ nanowastes generated by the sodium and potassium chlorate industries in China, for example, are typically adsorbed with the carcinogenic heavy metal chromium(VI) (see Figure S1 in the Supporting Information).[7,8] As illustrated in Figure 1, landfill after solidification is the conventional method for disposing of toxic Cr^{VI} sludge.[9,10]

Herein we report an effective strategy for disposing of the above-mentioned Cr^{VI}-containing nanowastes. Transforming Mg(OH)$_2$ nanoparticles into bulk materials releases the adsorbed Cr^{VI} into solution. This Cr^{VI}-containing solution can subsequently be recycled in the chlorate process and the detoxified solids can potentially be reutilized as additives in other applications, such as in ceramics, paint, flame-retardant engineering plastics, or lubricants. The present approach
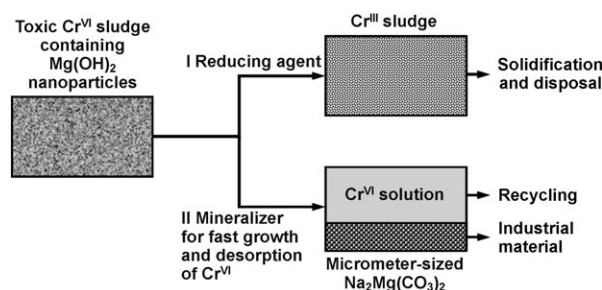

Figure 1. Disposal of Cr^{VI}-containing sludge (I: The conventional process; II: the new route proposed in this study).

could lead to alternative solutions for dealing with other nanosized pollutants.

Typical Cr^{VI}-containing nanowastes consist of about 50% water, 2048 mg kg^{-1} of Cr^{VI}, 30% of 20-nm Mg(OH)$_2$, and 16% of 100-nm CaCO$_3$. The pH of the waste is around 9. The viscous solid is quite difficult to separate from chromate solutions by any centrifugation, washing, or filtration methods. However, addition of a suitable mineralizer to the nanowastes during hydrothermal coarsening might accelerate the crystal-growth speed of nanoparticles[11] or transform them into compounds with reduced surface adsorption properties. A systematic survey of suitable mineralizers was therefore conducted (Table S1 in the Supporting Information). The most appropriate mineralizer was found to consist of 0.5 M Na$_2$CO$_3$ and 1.5 M NaHCO$_3$ (1:10, w/v; mineralizer A) as: 1) it provides the highest removal efficiency of Cr^{VI}, and 2) the mineralizer remaining in the supernatant solution can be transformed into essential reagents for industrial recycling (see Supporting Information).

Figure 2 shows a comparison of the settling velocity and grain size of three typical samples. The original nanowaste contains a significant amount of lamellar Mg(OH)$_2$ nanocrystals, which do not settle easily from the solution (Figure 2 a,d). Hydrothermal coarsening in pure water did not alter the growth and settling velocity of these lamellar nanocrystals appreciably (Figure 2 b,e), thereby indicating that the Mg(OH)$_2$ phase in the mud can remain stable on a nanometer scale for extended time periods under naturally occurring conditions. However, after hydrothermal coarsening of the nanowaste with mineralizer A (NaHCO$_3$ + Na$_2$CO$_3$), the solids settled to the bottom of the test tube in only 15 min. A subsequent scanning electron microscope (SEM) observation revealed that the nanocrystals had already grown into microsized structures (Figure 2 c,f). The amount of chromium remaining in the solid after treatment was determined to be 58, 42, and 0.64%, respectively.

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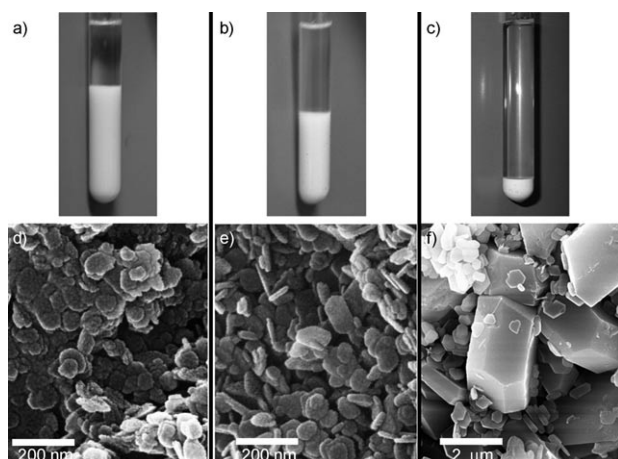Beijing 100080 (China)

Figure 2. The settleability test and SEM images of the samples: a) and d) original sample; b) and e) sample coarsened in distilled water at 180°C for 24 h; c) and f) sample coarsened in mineralizer A (NaH-CO$_3$ + Na$_2$CO$_3$) at 180°C for 24 h. The solid/liquid ratio used in the settleability test was 1 g/10 mL, with a settling time of 3 h. The leaching concentration of Cr^{VI} of the third precipitate was only 0.042 mg L^{-1}, far below the standard of environmental protection technical specifications for treatment of chromium residues in China (HJ/T 301-2007, 0.5 mg L^{-1}).
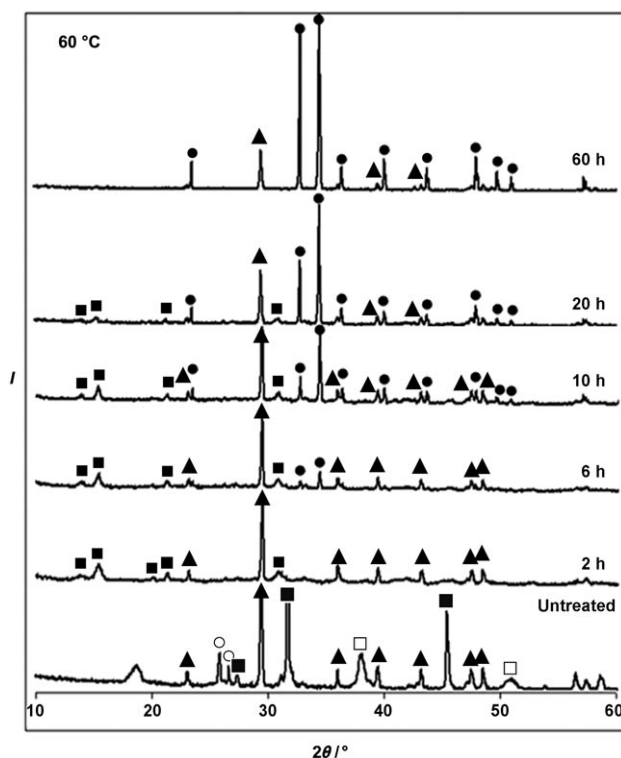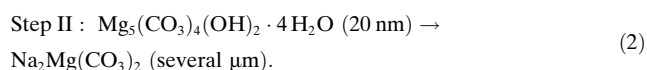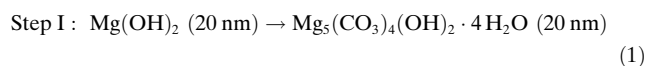
X-ray diffraction (XRD) analysis revealed that the Mg(OH)$_2$ phase is changed completely into Na$_2$Mg(CO$_3$)$_2$ when coarsened with mineralizer A at 180°C for 3 h. SEM observations revealed that this Na$_2$Mg(CO$_3$)$_2$ is well crystalline with a crystal size about hundreds times greater than that of Mg(OH)$_2$. Time series experiments were carried out at relatively low temperatures in order to follow the evolution of the phase transformation of Mg(OH)$_2$ in more detail (the CaCO$_3$ phase remained unchanged during the whole process; see Figure 3). The elementary phase-transformation steps are shown in Equations (1) and (2).

$$\text{Step I}: \ \text{Mg(OH)}_2 \ (20\,\text{nm}) \rightarrow \text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\,\text{H}_2\text{O} \ (20\,\text{nm}) \tag{1}$$

$$\text{Step II}: \ \text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\,\text{H}_2\text{O} \ (20\,\text{nm}) \rightarrow \\ \text{Na}_2\text{Mg(CO}_3)_2 \ (\text{several } \mu\text{m}). \tag{2}$$

As shown in Figure 4 and Table 1, we found that Cr^{VI} desorption is closely related to the generation of Mg$_5$-(CO$_3$)$_4$(OH)$_2$·4H$_2$O (step I) but independent of the phase transformation from Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O to Na$_2$Mg-(CO$_3$)$_2$ (step II). This desorption process could be related to the surface charge: The positive charge on the surface of the

Figure 3. Time series XRD analysis of the samples treated hydro-thermally in mineralizer A at 60°C. (□ Mg(OH)$_2$, ▲ CaCO$_3$, ■ Mg$_5$-(CO$_3$)$_4$(OH)$_2$·4H$_2$O, ● Na$_2$Mg(CO$_3$)$_2$, ○ KClO$_3$, ■ NaCl). The Mg(OH)$_2$ nanophase disappeared within 2 h, with concomitant appearance of an intermediate nanophase (Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O). The final phase (Na$_2$Mg(CO$_3$)$_2$) formed within 6 h and coexisted with Mg$_5$-(CO$_3$)$_4$(OH)$_2$·4H$_2$O. After 60 h, all Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O had been completely transformed into micrometer-sized Na$_2$Mg(CO$_3$)$_2$. The same phase-transformation mechanism was found for temperatures ranging from 40 to 180°C (Figure S2 in the Supporting Information).
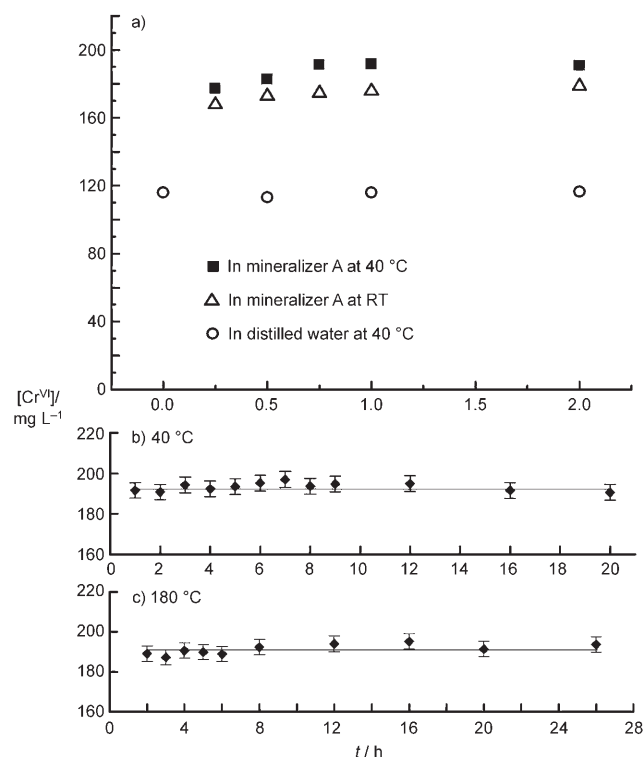

Figure 4. a),b) A comparison of the Cr^{VI} concentrations in supernatant liquids treated with distilled water and mineralizer A. Cr^{VI} could not be successfully extracted in the absence of mineralizer. The extracted Cr^{VI} reached a maximum (90%) within one hour upon treatment with mineralizer at 25 or 40°C; after that no noticeable change was observed. At this time all the Mg(OH)$_2$ had been completely replaced by Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O (Table 1). c) The same desorption behavior was found when the waste was coarsened in mineralizer A at temperatures between 60 and 180°C.

Table 1: Phase composition of the sediments after treatment at 25 and 40°C for different times.

t [min]	25°C	40°C
15	□ ■ ▲	□ ■ ▲
30	□ ■ ▲	□ ■ ▲
45	□ ■ ▲	□ ■ ▲
60	□ ■ ▲	■ ▲
120		■ ▲

□ $Mg(OH)_2$, ■ $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, ▲ $CaCO_3$.

$Mg(OH)_2$ nanomaterial can either facilitate the adsorption of CrO_4^{2-} anions or prevent the aggregation of the nanophase.[12] Upon addition of HCO_3^- anion, the $Mg(OH)_2$ lamellar nanocrystals can react rapidly with the ions by surface adsorption, which results in the formation of a $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ phase with a similar size and shape and desorption of CrO_4^{2-} anion. It is worth mentioning that the aggregation state of lamellar $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ is totally different from that of $Mg(OH)_2$ (Figures 2e and 5c), which is also indicative of a decrease of the surface charge after the reaction.
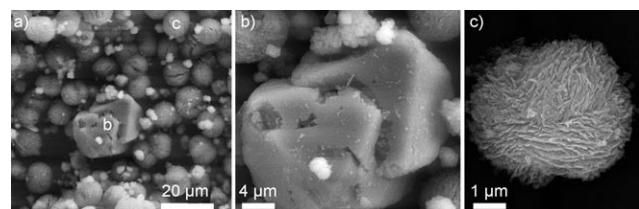

Figure 5. SEM images of the sample coarsened in mineralizer A for 6 h at 60°C: a) an intermediate state containing both $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ microspheres and $Na_2Mg(CO_3)_2$ microcrystals; b) a typical $Na_2Mg(CO_3)_2$ microcrystal ("b" in Figure 5a); c) a typical $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ microsphere highly aggregated by lamellar nanostructures ("c" in Figure 5a; see also Figure S3 in the Supporting Information).

Both extensive SEM observations and an analysis of the XRD peak broadening with the Scherrer equation reveal that the $Na_2Mg(CO_3)_2$ phase is an intrinsic bulk material (at least several hundreds of nanometers in width), which suggests that the growth rate of $Na_2Mg(CO_3)_2$ is extremely high. We propose a collective phase-transformation from $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ microspheres to $Na_2Mg(CO_3)_2$ microcrystals.[13, 14] As illustrated in Figure 6a, while the nucleation probability of $Na_2Mg(CO_3)_2$ may be small at the beginning, once $Na_2Mg(CO_3)_2$ has nucleated on the $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ microsphere it is likely to follow the collective-phase-transformation mechanism and propagate rapidly until the whole $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ microsphere has changed into a $Na_2Mg(CO_3)_2$ microcrystal (Figure 6b).[15] Further research is still needed, however, to elucidate the underlying mechanism.

The mechanism of Cr^{VI} removal during the whole process is summarized in Figure 7. This process involves 1) desorption of Cr^{VI} from the surface of the nanoparticles due to a phase transformation, and 2) efficient separation of the Cr^{VI}-con-
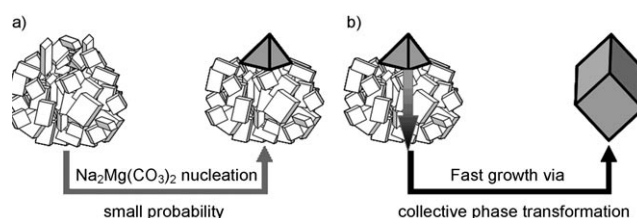

Figure 6. Collective-phase-transformation mechanism: The entire $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ microsphere becomes a $Na_2Mg(CO_3)_2$ microcrystal by rapid propagation from the nucleus.
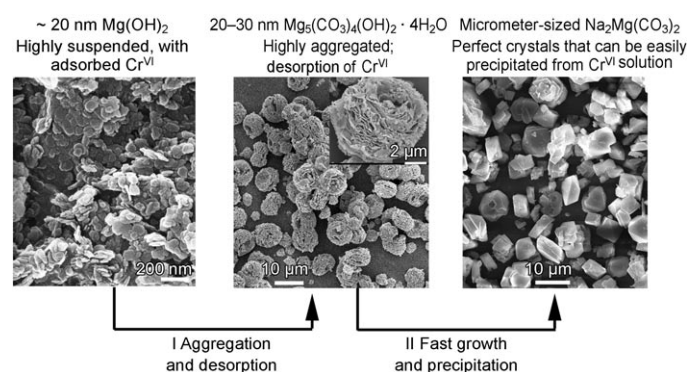

Figure 7. Summary of the mechanism of Cr^{VI} removal.

taining liquid from the solid due to fast crystal growth. Although the desorption of Cr^{VI} is almost complete during step I, complete separation of the Cr^{VI} solution from the $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ microspheres is still very inefficient due to the fact that Cr^{VI} oxyanions are contained in the loose and incompact nanoaggregates. The settling velocity of the solid produced is clearly enhanced after the fast crystal growth in step II, and the effect of separation of the supernatant liquid is also greatly improved (Figure S4 in the Supporting Information). In fact, due to the thermodynamic effect, nanoparticles can either spontaneously grow in size or, if they are highly reactive, form new compounds. In many natural systems, however, nanophases can remain stable on a nanometer scale for extended time periods,[16] therefore accelerating the reaction and growth rate of nanowastes is crucial for the effective transformation of specific nanowastes. In this work we have artificially accelerated the reaction and growth of $Mg(OH)_2$ nanomaterials and have demonstrated the potential of this concept. The addition of $NaHCO_3/Na_2CO_3$ mineralizer has been shown to be successful in dealing with ton-scale Cr^{VI}-containing $Mg(OH)_2$ nano-sludge produced by a chlorate plant (see "Pilot-scale tests" in the Supporting Information).

In summary, we have shown that Cr^{VI}-containing nanowastes can be transformed into nontoxic, micrometer-sized, superfine powders by phase transformation and rapid growth of $Mg(OH)_2$ nanoparticles in a process that releases Cr^{VI} into solution. This waste-disposal strategy has been proved to be successful in dealing with ton-scale nanowastes. Compared with more commonly used methods for detoxifying chromate-bearing sludge, which usually involve reducing Cr^{VI} to Cr^{III},

Communications

this work proposes a new method for recycling Cr^{VI} and reutilizing the nontoxic solid waste produced.

Experimental Section

The Cr^{VI}-bearing nanowaste (FJ0001) used in this experiment was obtained from a chlorate factory in Fujian Province (China). During the process of electrolyzing NaCl into NaClO$_3$ or KClO$_3$, Na$_2$Cr$_2$O$_7$ is added to the electrolyte solution in order to obtain high current efficiency.[7] The solid waste produced contains nanoscale Mg(OH)$_2$ and CaCO$_3$ as well as a large amount of carcinogenic chromate.[8] Parallel experiments were conducted to confirm the effects of hydrothermal treatment, temperature, and time on the desorption of Cr^{VI}. In general, 3 g of initial nanowaste (1.5 g of nanowaste on a dry basis and 1.5 mL of water) and 13.5 mL of hydrothermal solution (NaHCO$_3$ + Na$_2$CO$_3$; 1:10, w/v) were mixed in a 20-mL, Teflon-lined, stainless steel autoclave and stirred with a glass rod to obtain an even dispersion. All chemicals were reagent grade. The autoclaves were then sealed and heated to the predetermined temperatures for a preset time and were then taken out of the oven and quenched to room temperature. After coarsening, the mixture settled into two distinct layers: a clear yellow supernatant layer and a bottom layer with yellowish precipitates which could be rinsed until it became white. An aliquot of supernatant solution was sampled for the Cr^{VI} determination, whereas the precipitates were centrifuged and rinsed three times with distilled water, then dried and ground into a powder for analysis by XRD, SEM, and total Cr and Cr^{VI} leaching tests.

XRD was used to identify the phases and average particle sizes of the samples. Diffraction data were recorded with a PANalytical X'Pert PRO diffractometer with Cu$_{K\alpha}$ radiation (45 kV, 40 mA) in the continuous scanning mode. The 2θ scan range was from 5° to 85° in steps of 0.017° with a collection time of 20 s per step. The average crystallite size was calculated from the peak broadening using the Scherrer equation. SEM analyses of samples were performed with a JSM-6700F scanning electron microscope equipped with an Oxford-INCA energy dispersive X-ray (EDX) spectroscope. The total Cr content in the solid was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Jobin Yvon Ultima2), which has a detection limit of 0.5 μg kg^{-1} and a precision of 1 mg L^{-1}. The concentration of Cr^{VI} in the supernatant liquid and the leaching of Cr^{VI} from the solid product were determined by the 1,5-diphenylcarbohydrazide spectrophotometric method (GB 7467 and GB/T 15555.4). Thus, Cr^{VI} was treated with 1,5-diphenylcarbo-hydrazide in an acidic medium and the resulting product quantified at 540 nm with a spectrophotometer. The detection limit and reproducibility of this method were estimated to be 0.1 μg L^{-1} and 0.6%, respectively. The extraction procedure for leaching Cr^{VI} was performed according to the sulfuric acid and nitric acid method (HJ/T 299-2007).

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[2] Nanowaste refers to industrial sludge containing nanoparticles.

[3] Mg(OH)$_2$ nanomaterial is normally generated in the brine purification step of the sea-salt raw material used in the chlor-alkali and chlorate industries[4] where NaOH and Na$_2$CO$_3$ are introduced to remove the Mg^{2+} and Ca^{2+} impurities.[5] The sludge generated contains a significant amount of 20-nm Mg(OH)$_2$ nanoparticles, which can adsorb the Cr^{VI} that is added intentionally to maintain the current efficiency during the electrolysis of NaCl.

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[12] The initial pH of the nanowaste is around 9, which is less than the isoelectric point of Mg(OH)$_2$ (approx. 11.9), therefore the Mg(OH)$_2$ nanomaterial in the nanowaste is positively charged.

[13] F. Huang, J. F. Banfield, *J. Am. Chem. Soc.* **2005**, *127*, 4523–4529.

[14] The collective movement of atoms is a new phase-transformation kinetic model. This model proposes that once a nucleus is formed, the boundary of the new phase will propagate rapidly until a surface or another propagating phase front is encountered.[13]

[15] Na$_2$Mg(CO$_3$)$_2$ is slightly soluble in mineralizer A solution (approx. 30 mg L^{-1}). As shown in Figure 5b, Na$_2$Mg(CO$_3$)$_2$ can grow to 20 μm within 6 h, thus suggesting that the growth rate of Na$_2$Mg(CO$_3$)$_2$ crystals must be of the order of several micrometers per hour. The solubility of a similar, slightly soluble material, for example ZnS, is around 750 mg L^{-1} in 4 M NaOH. The growth rate of ZnS in 4 M NaOH at 100 °C is only 0.02 nm h^{-1} via exclusive oriented attachment (OA) growth, or 0.0026 nm h^{-1} via Ostwald ripening (OR) growth.[11] The growth rate of Na$_2$Mg(CO$_3$)$_2$ is therefore extremely high. Such a high rate is not likely to be possible by oriented attachment growth due to the relatively large grain size or by classical Ostwald ripening growth due to slow precipitation/dissolution at the particle/matrix interface.

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