Copper aluminate spinel in the stabilization and detoxification of simulated copper-laden sludge

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This study aims to evaluate the feasibility of stabilizing copper-laden sludge by the application of alumina-based ceramic products. The processing temperature, material leaching behaviour, and the effect of detoxification were investigated in detail. CuO was used to simulate the copper-laden sludge and X-ray Diffraction was performed to monitor the incorporation of copper into the copper aluminate spinel (CuAl12O14) phase in ceramic products. It was found that the development of CuAl12O14 increased with elevating temperatures up to and including 1000 °C in the 3 h short-sintering scheme. When the sintering temperature went above 1000 °C, the CuAl12O14 phase began to decompose due to the high temperature transformation to CuAlO2. The leachability and leaching behaviour of CuO and CuAl12O4 were compared by usage of a prolonged leaching test modified from US EPA’s toxicity characteristic leaching procedure. The leaching results show that CuAl12O14 is superior to CuO for the purpose of copper immobilization over longer leaching periods. Furthermore, the detoxification effect of CuAl12O4 was tested through bacterial adhesion with Escherichia coli K12, and the comparison of bacterial adhesion on CuO and CuAl12O4 surfaces shows the beneficial detoxification effect in connection with the formation of the CuAl12O4 spinel. This study demonstrates the feasibility of transforming copper-laden sludge into the spinel phase by using readily available and inexpensive ceramic materials, and achieving a successful reduction of metal mobility and toxicity.

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1. Introduction

The discharge of hazardous metals into receiving waters is detrimental to human health and the environment. As a type of hazardous metal that is subject to potential bioaccumulation, copper may cause stomach and intestinal distress, liver and kidney damage, and anaemia in humans (Gardea-Torresdey et al., 1996). Copper is present in the wastewater generated from printed circuit board manufacturing, electroplating, wire drawing, copper polishing, paint production, wood preservatives and printing operations. Common strategies that are chosen to remove hazardous metals from wastewater include physicochemical processes such as precipitation, coagulation, reduction, ion exchange and membrane processes (Park et al., 2005). However, the treatments mentioned above always result in the production of large amounts of hazardous-metal bearing sludge which requires additional treatment.

At present, sludge with hazardous metal residues needs to be disposed of in controlled landfills. However, the high cost of this strategy, combined with the limited number of landfills capable of accepting highly toxic metal wastes, has made the development of effective and economical treatment technologies essential. Many investigators have attempted to immobilize toxic metals using sorbents or cements and then correlating the performance directly with metal leachability (Kapoor and Viraraghavan, 1996; Lin et al., 1998; Bailey et al., 1999). However, solidification/stabilization technologies via sorption or cementation mechanisms are not generally successful in the prevention of leaching in acidic environments, i.e. a pH value less than 4.0 (Bonen and Sarkar, 1995; Yousuf et al., 1995).

Based on phase transformation at high temperature, attempts to stabilize radioactive waste in vitrified glass or ceramic materials have been carried out through a variety of thermal treatments (Lewis et al., 1993, 1994; Wronkiewicz et al., 1997; Wang et al., 2005; Shih and Leckie, 2007). However, the products are not reusable due to their radioactive nature. A similar thermal treatment process with relatively lower firing temperatures (900–1600 °C) compared to vitrification may be helpful in promoting the effective incorporation of waste materials into ceramic products, such as bricks, tiles, refractories, and aggregates (Teixeira da Silva et al., 1998; Shih and Leckie, 2007). Converting hazardous sludge to ceramic products via well-controlled thermal treatment can remove hazardous metals from the waste stream and enable them to become reusable. The leachability of hazardous metals can be reduced because of the change of mineral phase after thermal treatment. Shih et al. (2006a,b) successfully stabilized simulated nickel sludge by sintering with alumina, hematite and kaolinite.
as the ceramic raw materials. They reported significant reduction of nickel leachability from the spinel phases of the products, compared to the phase of nickel oxide.

It was previously reported that copper could be incorporated into the products sintered from clay materials, but the incorporation mechanism and phase transformation pathway have not been discussed in detail (Wei et al., 2001). An equilibrium phase diagram for CuO-Al2O3 system was published (Wartenberg and von Reusch, 1935), and the formation of the copper spinel was obtained by calcining the co-precipitation mixture of copper and aluminium hydroxide (Gadalla and White, 1964). Jacob and Alcock (1975) investigated the thermodynamics of copper aluminate spinel (CuAl2O4) formation and delineated the equilibrium phase diagram of the CuO-CuO-Al2O3 system. The above equilibrium studies have provided a great opportunity to highlight the interaction between copper oxide and alumina at high temperatures. It is thus anticipated that the incorporation of copper-laden sludge into ceramic materials through thermal treatment may be a promising strategy for stabilizing hazardous copper wastes. However, the potential of initiating copper spinel formation in the industrial short-sintering scheme of ceramic products (i.e. tiles, insulators, refractories) will require further investigation.

As an environmentally benign product, the material’s surface should be capable of supporting microbial activities. The adhesion of bacteria is usually the key factor for developing biofilm on material surfaces, which later becomes the major support basis for other biological growth. Due to the strong aquatic toxicity, copper oxide has been used in paints for marine environments to reduce the formation of biofilm on material surfaces. Copper-based paint may work as a selective medium for organisms by creating a toxic boundary layer at the surface of the biocides leach out (Evans, 1981; Douglas-Helders et al., 2003). The use of copper-based paints to prevent biofilm development and a biofouling effect has gained increasing attention due to its environmental impact of releasing toxic copper ions into aquatic ecosystems (Chamberlain et al., 1988; Katranitsas et al., 2003). It has been reported that concrete sewer pipes coated with copper oxide exhibit antimicrobial characteristics and can achieve 99% inhibition against the bacteria (Hewayde et al., 2007). Toxicities of compounds can be measured singly and in mixtures of various complexities, using acute toxicity bioassays (Fernández-Alba et al., 2001, 2002). Reaction evaluation on the surfaces of soda-lime glass (silica-based), CuAl2O4 and CuO pellets. The culture solution was prepared with 10 g of peptone bacteriological (Beijing Chemical Works, 44075-2H, 250 g), 10 g of NaCl (Riedel-deHaen) and 5 g of yeast extract into 20 mm pellets at 650 MPa to ensure consistent compaction of powder sample in readiness for the sintering process. After sintering, the samples were air-quenched and ground into powder for XRD analysis and the leaching test.

Phase transformations during sintering were monitored by XRD. The diffraction patterns were collected using a Bruker D8 diffractometer (Bruker Co., Ltd.) equipped with Cu X-ray tube operated at 40 kV and 40 mA. Scans were collected from 10° to 90° 2θ, with a step size of 0.02° and a counting time of 1 s step⁻¹. Phase identification was executed by matching XRD patterns with the powder diffraction files (PDF) database of the International Centre for Diffraction Data (ICDD). The leachability of the pure phase was tested using a leaching experiment which is a leaching procedure modified from the US EPA SW-846 Method 1311 – Toxicity Characteristic Leaching Procedure (TCLP) with a pH 2.9 acetic acid solution (extraction fluid # 2) as the leaching fluid. Each leaching vial was filled with 10 mL of TCLP extraction fluid and 0.5 g of powder. The leaching vials were rotated end-over-end at 60 rpm for agitation periods of 0.75–22 d. At the end of each agitation period, the leachates were filtered with 0.2 μm syringe filters, the pH was measured and the concentrations of all metals were derived from ICP-AES (Perkin-Elmer Optima 3300 DV).

In this study, the bacterial adhesion experiment was carried out to first qualitatively observe the toxicity for CuAl2O4 surface. The Escherichia coli K12 bacteria strain was chosen for use in this adhesion evaluation on the surfaces of soda-lime glass (silica-based), CuAl2O4 and CuO pellets. The culture solution was prepared with 10 g of peptone bacteriological (Beijing Chemical Works, 44075-2H, 250 g), 10 g of NaCl (Riedel-deHaen) and 5 g of yeast extract in 1 L of water. The glass material was taken from the microscope slides commonly designed for laboratory work, and it is an example of a non-toxic surface in the study of bacterial adhesion. The CuO powder was pressed into pellets and heated at 950 °C for 3 h. This was to effectively enhance the pellet strength and surface smoothness to facilitate the experimental needs, but also aimed to maintain the phase status (CuO) of the material. The mixture of CuO and CuAl2O4 precursor (Cu/Al molar ratio = 1:2) was also pressed into pellets and heated until CuAl2O4 was observed as the single phase in the product (990 °C for 20 d). Both CuO and CuAl2O4 pellets derived from the above processes were later polished by the diamond lapping films progressively down to a diamond grit size of 0.1 μm. Measurement of the surface roughness of glass, CuO and CuAl2O4 samples was conducted using a JPK Instruments atomic force microscope (AFM) equipped by silicon-cantilevers with a force constant of 0.1 N m⁻¹. Height images (40 × 40 μm²) were used to calculate the roughness measurement based on the arithmetic average. Bacteria adhered on the substrata were stained with SYTO9 and observed using a fluorescence microscope (Nikon Eclipse E600).

2. Materials and methods

When thermally treated, the metal components of sludge are usually first transformed into oxide forms and thus CuO (Sigma Aldrich) was used to simulate the thermal reaction of copper-laden sludge. Experiments were carried out by firing the mixture of CuO and γ-Al2O3 precursor. The γ-Al2O3 was prepared from HiQ-7223 alumina powder (Alcoa), which has a reported average particulate size (d50) of 54.8 nm. The HiQ-7223 alumina was confirmed by X-ray Diffraction (XRD) to be the boehmite phase (AIIOH; ICDD PDF # 74-1875), and after heat treatment at 650 °C for 3 h it was successfully converted to γ-Al2O3 with an XRD crystallite size of 2–5 nm (Zhou and Snyder, 1991; Wang et al., 2005). The γ-Al2O3 precursor, CuO and CuAl2O4 were mixed to a total dry weight of 200 g at the Cu/Al molar ratio of 1:2, together with 1 L of deionized water for ball milling of 18 h. The slurry samples were then dried and homogenized by mortar grinding. The derived powder was pressed into 20 mm pellets at 650 MPa to ensure consistent compaction of the powder sample in readiness for the sintering process. After sintering, the samples were air-quenched and ground into powder for XRD analysis and the leaching test.

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3. Results and discussion

3.1. Copper spinel formation

By sintering the mixture of CuO and γ-Al2O3, copper incorporation may proceed under a recrystallization reaction as follows:
CuO + γ-Al2O3 → CuAl2O4 (1)

It has been reported that the incorporation ability of γ-Al2O3 for nickel is affected by the sintering temperature (Shih et al., 2006a,b). To investigate the effective temperature for alumina content to incorporate copper into the CuAl2O4 in the practice of sintering construction ceramic products, a 3 h short-sintering scheme at temperatures ranging from 650 to 1150 °C was conducted. According to the database of the CuAl2O4 XRD pattern (ICDD PDF # 33-0448), its two major peaks are located at 2θ = 36.868° and 31.294°, corresponding to the diffraction planes of (3 1 1) and (2 2 0) respectively. The result reveals that the sample sintered at 750 °C developed a distinguishable CuAl2O4 crystalline phase as shown in Fig. 1a. Jacob and Alcock (1975) observed the formation of the CuAl2O4 in their equilibrium thermal experiment (for 24 h) and reported the spinel formation temperature to start at 612 °C.

However, when compared to the results observed in our short-sintering experiment, it was discovered that an effective sintering period for industrial application to incorporate copper into CuAl2O4 in ceramic products should be at least above 750 °C. Since the solid state reaction is usually affected by both thermodynamic conditions and the diffusion process, this comparison may further suggest that spinel formation at temperatures below 750 °C is largely limited by the prevailing slow diffusion although it is thermodynamically feasible at temperatures above 612 °C. Below 750 °C, the CuAl2O4 phase formed by the short-sintering scheme may only be limited at the grain boundary of reactants, and the very small quantity of such phase in the system was not reflected in the XRD results.

Two 2θ ranges of the XRD pattern (2θ = 36.4–37.4° and 31.0–32.0°) were selected to further observe the peak intensity development to represent the CuAl2O4 spinel product generated from the system at elevated temperatures (Fig. 2). Fig. 2a observes the crystallization of CuAl2O4 developed from the CuO + γ-Al2O3 precursor within the 2θ range of 36.4–37.4° at different sintering temperatures. Although there was a distinguishable CuAl2O4 phase in the 750 °C sintered sample, the substantial growth of CuAl2O4 in the system was observed to be at above 850 °C, which may indicate the energy needed to overcome the major diffusion barrier in the system. Below 1000 °C, the peak intensity of the CuAl2O4 phase increases as the temperature increases. However, at sintering temperatures higher than 1000 °C, the peak intensity of the CuAl2O4 phase was found to decrease with elevated temperatures.

The XRD patterns within the 2θ range of 31.0–32.0° (Fig. 2b) show that the decrease of CuAl2O4 at higher temperatures was due to the formation of another new Cu–Al oxide phase, cuprous aluminate delafossite (CuAlO2; ICDD PDF # 75-2356). Fig. 2b has further verified the optimal formation temperature of CuAl2O4 at 1000 °C, and the phase transformation to CuAlO2 at higher temperatures was observed by the (0 0 6) diffraction plane signal of CuAlO2 at 2θ around 31.63°. Since the decrease of CuAl2O4 at higher temperatures was accompanied with a corresponding increase of CuAlO2 in the system, it is suggested that the formation of CuAlO2
occurred immediately after the decomposition of CuAl2O4, or went through structural transformation by discharging the excessive aluminium and oxygen from the crystal structure. Nevertheless, both phase transformation mechanisms indicate that the opportunity of immobilizing copper from the Al–O incorporated structures is small when this phase transformation process takes place at high temperatures. Together with the interaction between unreacted CuO and Al2O3 (Jacob and Alcock, 1975), the CuAlO2 formation mechanisms at temperatures above 1000 °C can be organized in the following way:

\[
\begin{align*}
2\text{CuAl}_2\text{O}_4 & \rightarrow 2\text{CuAlO}_2 + \text{Al}_2\text{O}_3 + 0.5\text{O}_2 \\
2\text{CuO} & \rightarrow \text{Cu}_2\text{O} + 0.5\text{O}_2 \\
\text{Cu}_2\text{O} + \text{Al}_2\text{O}_3 & \rightarrow 2\text{CuAlO}_2
\end{align*}
\]

3.2. The leaching mechanisms

To investigate the effect of copper immobilization after the incorporation by the spinel structure, the preferred method was to first compare the leachability of single phase samples under the same leaching environment. Therefore, this study prepared a leaching experiment sample with CuAl2O4 as the only phase appearing in the sample. From the incorporation efficiency experiment, it was observed that 1000 °C as the sintering temperature could attain the highest yield of CuAl2O4 phase without initiating the formation of the CuAlO2 phase, although small amounts of reactants (Al2O3 and CuO) were still observed in the system. To ensure the complete transformation of reactants to the product phase (CuAl2O4), a longer sintering time (20 d) was used to facilitate reaction equilibrium. Moreover, the sintering temperature of 990 °C, which is slightly less than 1000 °C, was chosen to further prevent the generation of the CuAlO2 phase during the prolonged sintering process. The XRD pattern in Fig. 1b shows the success achieved by preparing the CuAl2O4 sample, where no peak of CuO or Al2O3 reactant phase was found in the pattern.

Samples used in the leaching test were ground into powder and measured to ascertain the BET surface area to yield values of 1.35 m² g⁻¹ for CuAl2O4 and 0.17 m² g⁻¹ for CuO. The pH values are shown in Fig. 3a, which reveals the greater pH increase of CuO leachate. Within the first few days, the pH of CuO leachate experienced a significant increase which was then maintained at around 4.7–4.9 throughout the rest of the leaching period. In contrast, the pH of the CuAl2O4 leachate was maintained at the beginning value of its leaching fluid throughout the entire leaching period. The increase of leachate pH may arise due to the dissolution of cations through ion exchange with protons in the solution. This is accompanied by the destruction of crystals at the solid surface by the acidic leaching fluid. The increase in leachate pH may indicate that CuO is more vulnerable to proton-mediated dissolution. On the other hand, CuAl2O4 (sintered from \(\gamma\)-Al2O3 + CuO) may show higher intrinsic resistance to such acidic attack, even with higher surface areas.

As the leaching for solid is likely dominated by surface reactions, it is expected to be proportional to sample surface area. In addition, since the same weight of sample (0.5 g) was always used, the total copper content in the sample, subject to the different copper phases, should also be normalized for comparison. Fig. 4 summarizes the amounts of leached copper from samples normalized with respect to the surface areas of tested solids. The copper in the CuO leachate was over 400 times higher than that in the CuAl2O4 leachate near the end of the leaching period. This confirms that the CuAl2O4 spinel phase has a higher intrinsic resistance to such acidic attack compared to the CuO phase and the sintering strategy designed for copper-laden sludge is proven to be beneficial in stabilizing copper. The curve in the small diagram further provides the details concerning the copper concentrations in the CuAl2O4 leachate.

Fig. 3. (a) pH values and (b) [Al]/[Cu] molar ratios of the leachates of the CuO and CuAl2O4 phases. The leaching solution was TCLP extraction fluid no. 2 (acetic acid solution) with a pH of 2.9. Each leaching vial was filled with 10 ml of extraction fluid and 0.5 g of powder sample, and then rotated end-over-end between 0.75 and 22 d.

Fig. 4. Normalized copper concentrations in the leachates of CuO and CuAl2O4. The surface area of CuO powder is 0.17 m² g⁻¹ and the surface area of CuAl2O4 is 1.35 m² g⁻¹. The leaching solution was TCLP extraction fluid no. 2 (acetic acid solution) with a pH of 2.9. Each leaching vial was filled with 10 ml of extraction fluid and 0.5 g of powder samples, and then rotated end-over-end between 0.75 and 22 d. The curve in the small diagram further provides the details concerning the copper concentrations in the CuAl2O4 leachate.
When the pH of the CuO leachate reached ~4.9, the leaching of CuO stabilized at a copper concentration of ~2500 mg L$^{-1}$ ($\approx 10^{-3.4}$ M) in the leachate. As a general assumption of cation-proton exchange mechanism, the destruction of copper oxide by the acidic attack of the solution can be expressed as:

$$\text{CuO}_{(s)} + 2\text{H}^+_{(aq)} \rightarrow \text{Cu}^{2+}_{(aq)} + \text{H}_2\text{O}$$  \hspace{1cm} (5)

However, the concentration of copper ions in the solution $[\text{Cu}^{2+}_{(aq)}]$ is also limited by the potential precipitation/dissolution reactions, such as in respect to $\text{Cu(OH)}_{2(s)}$:

$$\text{Cu(OH)}_{2(s)} \rightarrow \text{Cu}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)}$$  \hspace{1cm} (6)

where the solubility constant ($K_{sp}$) of Eq. (6) is $10^{-19.25}$ (Stumm and Morgan, 1996). At pH 4.9, the product of $[\text{Cu}^{2+}_{(aq)}] \times [\text{OH}^-_{(aq)}]^2$ was found to be $10^{-19.5}$, which is very close to the $K_{sp}$ of $\text{Cu(OH)}_{2(s)}$. This result indicates that the system was very close to the saturation of $\text{Cu(OH)}_{2(s)}$ and the stabilization of copper concentration in the CuO leachate was likely controlled through the equilibrium with the $\text{Cu(OH)}_{2(s)}$ phase.

When leaching the CuAl$_2$O$_4$ phase, a “congruent dissolution” through the cation-proton exchange reaction can be written as:

$$\text{CuAl}_2\text{O}_4_{(s)} + 8\text{H}^+_{(aq)} \rightarrow \text{Cu}^{2+}_{(aq)} + 2\text{Al}^{3+}_{(aq)} + 4\text{H}_2\text{O}$$  \hspace{1cm} (7)

Such congruent dissolution would result in a theoretical $[\text{Al}^{3+}_{(aq)}]/[\text{Cu}^{2+}_{(aq)}]$ molar ratio of 2.0 in the leachates. However, this ratio was observed at 0.75–0.80 in the leachate of CuAl$_2$O$_4$ as shown in Fig. 3b. Since the system was maintained in a more acidic environment (pH 3.2) and the copper concentration was much lower than that of the CuO leachate, the copper concentrations in the leachates of CuAl$_2$O$_4$ were all considerably under-saturated regarding to the $\text{Cu(OH)}_{2(s)}$. The aluminium concentrations measured in the CuAl$_2$O$_4$ leachates were ~9.5 mg L$^{-1}$ ($\approx 10^{-3.45}$ M). The reaction of amorphous aluminium hydroxide precipitation/dissolution is:

$$\text{am } \text{Al(OH)}_{3(s)} \rightarrow \text{Al}^{3+}_{(aq)} + 3\text{OH}^-_{(aq)}$$  \hspace{1cm} (8)

where the solubility constant ($K_{sp}$) of Eq. (8) is $10^{-32.7}$ (Stumm and Morgan, 1996). The product of $[\text{Al}^{3+}_{(aq)}] \times [\text{OH}^-_{(aq)}]^3$ was found to be $10^{-35.9}$ and it did not reach the saturation ($[\text{Al}^{3+}_{(aq)}] \times [\text{OH}^-_{(aq)}]^3 = 10^{-32.7}$) of amorphous Al(OH)$_3(s)$ either. Therefore, this suggests that the leaching behaviour of CuAl$_2$O$_4$ in this experiment is likely to be an incongruent dissolution, where the majority of the Al–O bonds still remained on the CuAl$_2$O$_4$ spinel surface. Although some previous studies (Cailletieu et al., 2008; Ohlin et al., 2010) have further suggested the reorganization of remaining molecules in incongruent dissolution scenarios, the overall result indicates the existence of an Al-rich layer on the leached CuAl$_2$O$_4$ surface, which is beneficial for preventing the further leaching of Cu and may increase product durability.

### 3.3. Adhesion of E. coli

Since the density of bacteria adhering to the product surface may potentially be used to evaluate the results of metal detoxification, this study first conducted a qualitative comparison of bacterial adhesion on the substrata of the CuAl$_2$O$_4$ spinel, CuO and soda-lime (silica-based) glass. Experimental studies have suggested the importance of the physicochemical and thermodynamic properties of both the substrata and the bacterial cell surface during the process of bacterial adhesion (Van Loosdrecht et al., 1989; Sjollema et al., 1990; Vadillo-Rodriguez and Logan, 2006). In this study, a type of testing bacteria, E. coli K12, was cultivated in a solution with a pH of ~6.5 and all the substratum samples were collectively placed in the same solution for better comparison. Since surface roughness may impact bacterial adhesion (Brant and Childress, 2002), the tested surfaces of samples were polished using diamond lapping films and the roughness values were measured by AFM to be 2.3 ± 1.7, 491 ± 192 and 369 ± 90 nm for glass, CuAl$_2$O$_4$ and CuO, respectively. Fig. 5 shows the results from the comparison of E. coli bacterial adhesion on the surface of glass, CuAl$_2$O$_4$ and CuO after 18 h of bacterial cultivation. The amount of E. coli adhering to the glass surface visibly surpassed the amount on the surfaces of both the CuAl$_2$O$_4$ and CuO samples (Fig. 5a). However, due to the toxicity effect, no bacterial adhesion was found on the surface of the CuO substratum as shown in Fig. 5c. With much lower copper leachability as compared to CuO, the CuAl$_2$O$_4$ spinel clearly developed bacterial adhesion on the surface which showed its capacity to support microbial activities, although the level was lower than that of the glass substratum (Fig. 5b).

As the inhibition effect of copper oxide on biofouling has already been indicated (Evans, 1981; Balls, 1987; Chamberlain et al., 1988; Hodson and Burke, 1994; Douglas-Helders et al., 2003; Katranitsas et al., 2003; Hewayde et al., 2007), the comparison result of glass and CuO in this study is consistent with previous findings. Moreover, some studies suggested that the increase of nano-scale roughness of a surface increases bacterial adhesion (Shellenberger and Logan, 2002); other studies have demonstrated no significant relationship between surface roughness and bacterial adhesion (Li and Logan, 2004). In our work, the highest level of bacteria adhered to the glass surface, even with much lower roughness, thus indicating the dominant effect of substrata material. The growth of bacteria on the surface of the CuAl$_2$O$_4$ substratum suggests the successful detoxification of copper through the stabilization strategy of incorporating CuO into the aluminate spinel phase. Since the formation of a biofilm covering on a surface begins with the adhesion of a small number of bacteria, the results shown here provide direct evidence of the environmental friendliness of waste-incorporated ceramic products. Such information on the intrinsic properties of material is also important and beneficial when aiming to minimize the environmental impact even after the end of a product’s life.
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