Chapter 16
Aggregates and High Value Products

Abstract To the development of technologies for global environmental protection and resource conservation, CO_2 mineralization technologies are considered as an cleaner production in industries for high-level reuse of solid waste and solidification of CO_2 from exhaust gas. This chapter provides the performance and challenges of utilizing fresh solid wastes as aggregates in concrete blocks. To improve the performance of concrete with fresh solid waste, a newly developed process, i.e., accelerated carbonation, was introduced. Through the accelerated carbonation process, additional high value-added chemicals, such as precipitated calcium carbonate, precipitated silica, and adsorbent, can be also produced for further utilizations. Moreover, other applications of carbonated solid wastes, such as (1) marine blocks as artificial reefs for marine forests and (2) abiotic catalyst for enhanced humification, are illustrated.

16.1 Aggregates

16.1.1 Classification

Concrete is made of roughly 70–80% aggregate (sand and gravel), 10–15% cement, and 5–10% additives and water. Construction aggregate can be used to strengthen composite materials, such as concrete and asphalt concrete, for a myriad of uses ranging from railroad bases to housing foundations. In the concrete mixture, the volume of cementitious paste should be large enough to (1) fill up the voids between aggregate particles, and (2) provide excess cementitious paste to form paste films coating the aggregate particles [1]. This can avoid entrapment of air inside the concrete mixture, which might impair the strength and durability. However, an excess ratio of cementitious paste in concrete will form paste films, thereby lubricating the concrete mixture and attaining the required workability.

The aggregates for construction can be classified as two types:

- coarse aggregate (generally ranging from 9.5 to 37.5 mm), including gravel and crushed stone;
- fine aggregate (usually smaller than 9.5 mm), including sand and crushed stone.

Extensive studies have been conducted to evaluate the performance of the use of limestone as fine aggregates in concrete [2]. It was found that the addition of limestone to reduce the cementitious paste volume would improve not only the dimensional stability but also the tensile strength, stiffness, and durability of concrete [1]. Aside from limestone minerals, many industrial waste materials can potentially be used as economical and environmentally friendly sand substitutes for cementitious building products.

16.1.2   Fresh Solid Waste as Aggregates: Performance and Challenges

Recycled concrete aggregate (RCA), collected from old roads and buildings, has shown promise as an alternative to natural aggregate. Table 16.1 presents the various properties of RCA for replacement of natural aggregate in construction concrete. While RCA has similar gradation to the natural aggregate, RCA particles are more rounded in shape and have more fine particles broken off in L.A. abrasion and crushing tests [3]. This suggests that the use of RCA as a structural concrete should be viable because the performance of RCA concrete beams was still within standard specifications [3–6]. Furthermore, creep can be minimized by incorporating fly ash as either an additive or a replacement in concrete in the case of RCA utilization [6].

16.1.3   Carbonated Solid Wastes as Aggregates

Carbonated alkaline solid waste can function as construction aggregates to partially replace sand, gravel, and crushed stone. Therefore, they can be considered as an economic and environmentally friendly sand substitute for cementitious building products. Several studies have been carried out to evaluate the performance of utilizing carbonated solid wastes as aggregates, such as carbonated steel slag as a fine aggregate in concrete [7].

Fernández-Bertos et al. [8] suggested that the carbonated particles became coarser due to agglomeration, which should be beneficial for use in aggregate manufacturing. The formed $CaCO_3$ crystals in carbonated solid waste appear to reduce the free-CaO content and fill pore spaces of specimens, thereby exhibiting good soundness and enhanced compactness, respectively [9]. In addition,

Table 16.1 Various properties of recycled concrete aggregate for natural aggregate replacement [3–6]

Properties	Unit	Performance of RCA replacement[a]					Remarks
		RCA 100%	RCA 50%	RCA 30%	RCA 15%	NA	
Density	kg/m^3	2394	n.r.	n.r.	n.r.	2890	• RCA is approximately 7–9% lower than NA
Porosity and water absorption	%	4.0–5.2	n.r.	n.r.	n.r.	0.5–2.5	• NA has low water absorption due to low porosity • RCA has greater water absorption due to greater porosity
Crushing test	%	23–24	n.r.	n.r.	n.r.	13–16	• Higher values for RCA were observed
L.A. abrasion test	%	32	n.r.	n.r.	n.r.	11	• Impacted and crushed by steel balls to determine amount of fine particles that break down • Higher values for RCA were observed
Compressive strength	MPa	n.r.	29	31.7	32.7	38.6	• Decreases compressive strength • Greater midspan deflections under service load
Tensile strength (splitting)	MPa	n.r.	2.7	2.7	3.0	3.3	• Concrete with RCA has comparable splitting tensile strength
Modulus of rupture (MOR)	MPa	n.r.	8.9	9.0	9.7	10.2	• MOR of RCA was slightly less than that of conventional concrete
Modulus of elasticity	MPa	15–28	n.r.	n.r.	n.r.	26–33	• Modulus of elasticity of RCA (28-d) is lower up to 45% than NA concrete
Drying shrinkage	Micro strain	540–790	n.r.	n.r.	n.r.	275–590	• Creep can be minimized by incorporating fly ash whether as addition or replacement (in the case of RCA)

Note [a]*RCA* Recycled concrete aggregate; *NA* natural aggregate; *n.r.* not report

Monkman et al. [7] found that the 28-d strengths of the mortars made with the carbonated ladle slag sand were comparable to those with normal river sand mortars. It is revealed that the carbonated ladle slag can be successfully used as fine aggregates to prepare mortar in precast products, such as masonry units, paving stones, and hollow core slabs.

These materials can be further treated by carbonation curing to enhance the strength development (as discussed in Chap. 8). It thus suggests that accelerated carbonation should be used to manufacture alkaline solid wastes as building materials, with high early compressive strength and eligible soundness, along with the benefit of CO_2 capture at the same time.

16.2 High Value-Added Chemicals

16.2.1 Precipitated Calcium Carbonate (PCC)

Recently, research has focused on the production of precipitated calcium carbonate (PCC) from indirect carbonation of alkaline solid wastes because it can be a profitable refining method for solid wastes if the purity requirements for commercial PCC can be achieved. Calcium ($CaCO_3$) and magnesium ($MgCO_3$) carbonates, considered as high value-added chemicals, can be used as coating pigments and as fillers in the pulp, rubber, plastic, paper, and paint industries. They can offer opacity, high brightness, and improved printability due to its good ink receptivity [10–12]. Approximately 75% of the produced PCC can be used in the paper industry as a brightness coating and filler [13, 14]. It can serve as a replacement for more expensive pulp fiber and optical brightening agents to improve the quality and printing characteristics of paper, such as smoothness, gloss, whiteness, opacity, brightness, and color. In addition, PCC can be utilized as an additive and filler in construction materials. Companies in North America, the EU, and Australia are working on developing a similar process, which involves CO_2 capture by bubbling flue gases through saline water to produce solid carbonates as an aggregate material in cement [15].

Indirect carbonation of alkaline solid wastes can produce high-purity PCCs. The application potentials for the PCC produced from the indirect carbonation depend on the obtained purity and variety of the crystal structures. In most applications, the favored crystalline forms of PCC are the rhombohedral calcite type, the orthorhombic acicular aragonite type, and the scalenohedral calcite type [16]. Other physico-chemical properties of PCC, such as particle size distribution, specific surface area, morphology, and polymorphism, also play an important role.

For the process design of carbonation, it suggests that a reaction temperature higher than 80 °C is unfavorable to efficient CO_2 dissolution, although the conversion for the extraction reaction is enhanced at higher temperatures [17]. The precipitation of $CaCO_3$ is endothermic and feasible at temperatures above 45 °C, while the carbonation of Mg^{2+} ions should be possible only at temperatures over 144 °C [18]. Therefore, in the case of 80 °C, the formation of $MgCO_3$ could be neglected. One of the findings in the literature indicated that a maximum carbonation conversion of 70% can be achieved, with a PCC purity of up to 98% [18]. Similarly, a maximum carbonation conversion of 86% can be achieved under a CO_2

concentration of 10 vol.% at 30 °C after acetic acid extraction, with a PCC purity as high as 99.8% [19].

16.2.2   Precipitated Silica

Silica (quartz, SiO_2) can be high value-added materials if the purity of precipitates can reach the requirement. Depending on the degree of purity refinement, precipitated silica can be used in various types of applications, such as filler (after mining), smelting plants and gravel (after crushing), glass (after separation), ceramics (after grinding), solar cells (after acid wash), and semiconductors (after advanced processing). The precipitated silica can also be utilized in pesticides, detergents, tires, oral health products, creams, footwear, and plastics. For instance, in the application of tires, the silica can improve wet skid performance and provide lower rolling resistance, thereby saving the fuel usage [20].

Silica is commonly used as a coating pigment together with polyvinyl alcohol for matte inkjet papers [21]. However, current methods of silica production for pigment purposes are quite expensive, i.e., 800–1000 €/t, since the water glass (sodium silicate, Na_2SiO_3) is used as the raw material [21]. During indirect carbonation using acetic acid or ammonium chloride, silica gel can be formed and then separated via filtration before sequential carbonation [18]. It was observed that the produced silica should be qualified for inkjet paper coating, as a replacement for commercially precipitated silica [21].

16.2.3   Adsorbent

In indirect carbonation, solid residues (such as steel slag) after extraction step could be converted into sorbent materials via hydrothermal conversion. After the hydrothermal conversion, a material with a larger surface area and micropores can be produced. Therefore, it offers the potential to behave as a sorbent. Mineralogical investigation of the sorbent materials after hydrothermal conversion indicated that two zeolitic phases were formed:

- ferrierite ($Na_2Mg(Si_{15}Al_3)O_{36} \cdot 9H_2O$) and
- gmelinite ($Na_4(Si_8Al_4)O_{24} \cdot 11H_2O$).

It can provide the sorption potential for heavy metals and organic compounds [22]. Since aluminum is an essential component of aluminosilicate-based zeolites, the organic acids used for the calcium extraction from solid wastes should prevent the leaching of aluminum ions, which is the key consideration for the synthesis of zeolites.

16.3   Other Applications

16.3.1   Marine Blocks as Artificial Reefs for Marine Forests

Artificial reefs, exhibiting a high stability in seawater, have often been used to recover and develop seaweed beds in at least 40 counties [23–25]. Seaweed beds play several important roles in the following:

- water quality purification,
- biological production,
- sediment stabilization,
- prevention of trawlers from destroying seabed, and
- conservation of the detritus food chain and primary consumers.

The preservation and development of seaweed bed with such functions can contribute to the increase in catches of useful seafood and fishes.

Conventionally, the materials commonly used as artificial reefs are concrete blocks and fieldstones. As an alternative to concrete, large marine blocks (e.g., 1 m^3 in size) have been developed using steel slags and CO_2 without supplying cement. Several studies have been conducted to evaluate the performance of marine blocks on the growth of brown algae, such as *Ecklonia cava* [24]. The brown algae can form a community called "marine forest" in coastal waster at 2–25 depth, which can be used as nursery and breeding spaces for commercial fishes and other animals. Furthermore, JFE Steel Corporation in Japan manufactured marine blocks as artificial reefs for seaweed/coral breeding using carbonated steel slag. The formed $CaCO_3$ components (the same composition to shells and coral) can act as great breeding habitats for seaweed and coral. As a result, the seaweed adhered and grew on the marine block is much more than on normal concrete. It suggests that the marine blocks could form artificial reefs offering the same functions as natural rocky reefs.

16.3.2   Abiotic Catalyst for Enhanced Humification

Humification can occur naturally in soil or in the production of compost. It is considered the primary process to stabilize soil carbon and organic matter in the form of humic substances (i.e., humus). Humus has a characteristic of black or dark brown color. Application of biotic and abiotic humification for organic carbon stabilization has been of great significance in bio-organic waste disposal, particularly in the composting process [26, 27]. Most of the humus in soils has persisted for more than a hundred years, rather than have been decomposed to CO_2. Therefore, humus can be regarded as stable organic matter that has been protected from decomposition by microbial or enzyme. It usually is hidden and occluded inside small aggregates of soil particles or tightly attached to clays.

The humification theory predates a sophisticated understanding of soils. It was noted that Fe(III)- and Mn(IV)-oxide minerals could act as effective oxidants and substantially enhance the polycondensation of humic precursors [28]. It is significant for accelerating the transformation and stabilization of biowastes during composting. For instance, the carbonated steel slag (e.g., basic oxygen furnace slag, BOFS) usually contains high quantities of Fe(III)- and Mn(IV)-oxide minerals. It was found that the carbonated BOFS could substantially promote the formation of humic-like acids (HLAs) from humic precursors, such as amino acids, saccharides, and phenols, under ambient temperature [29]. For humification, it suggests that carbonated BOFS should be used instead of uncarbonated BOFS in the first place since uncarbonated slag has been linked to metal leaching issues. Accelerated carbonation has been shown to reduce the leaching of metals by orders of magnitude to make the slag environmentally benign [27, 30].

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