

## Review Article

# Recent Progress in Chemically Bonded Phosphate Ceramics

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Chemically bonded phosphate ceramics have made an excellent progress in the last 10 years and are poised to be one of the major inorganic room-temperature setting materials for nuclear, structural, dental, and prosthetic applications. They are also poised to be the first inorganic industrial coatings for fire and corrosion protection applications. In 2004 the author in his book, *Chemically Bonded Phosphate Ceramics*, presented general theory, compositions, methods of fabrication, and preliminary commercial products that appeared in the market ten years ago. This paper reviews that background and presents advances of last ten years with an emphasis on the recent applications in the nuclear field.

## 1. Evolution of Chemically Bonded Phosphate Ceramics

Discovery of ceramics has been concurrent with evolution of human civilization. Early ceramic tools used for hunting and self-defense, thatched mud houses for shelter, and earthenware used for cooking were the first products of survival that all used some binding mechanism to put particles together in a desired shape. Rocks, minerals, and dirt were readily available and hence they became the raw materials. Fire was known in early stages of civilization and fired products could be made easily. In spite of these advances in production of ceramics, their scientific understanding had to wait for development of science of materials. Thus, ceramic science is only few hundred years old, which now explains how the binding mechanisms work. High temperature diffusion of atoms between the particles and fusion of particles or chemical bonding are the two basic binding processes. Products of the first process are traditionally known as ceramics while those produced by the second process are cements.

High temperature treatment was used in fabricating almost all ceramics. Since granting of the first patent on Portland cement [1], however, significant efforts were invested in understanding the role of chemical bonding in production of cements. The ready acceptance of Portland cement as a building material indicates the importance of chemical bonding as an alternative to high temperature sintering. Simplicity of casting large shapes was a great technological

advancement over high temperature ceramics. From scientific viewpoint, Portland cement consists of noncrystalline binding phases, while most ceramics are identified by their dominant crystalline structure with an exception of glass that is noncrystalline but produced at high temperature. Thus dominance of noncrystalline binding phases in cements as against the crystal structure of ceramics distinguishes cements and ceramics.

During the last hundred years, the chemical bonding has gained importance in producing range of binders. Lessons learnt from Portland cement and polymer science led to chemical processes that yielded noncrystalline binding phases. Understanding how chemical bonds between neighboring particles hold together and form solid objects was the key to production of the first commercially available chemically bonded cement products [2, 3]. Wilson and Nicholson [4] generalized this concept to classify range of products that they named Acid-Base Cements (ABCs), a class within chemically bonded products.

As new ABCs were discovered, it was recognized that crystalline phases are not exclusive to ceramic structures but are also found in ABCs. Likewise detailed microstructural investigations revealed that noncrystalline phases can exist in ceramics. Such ceramics are known as glass ceramics. Thus the distinction between the structure of ceramics and cements is blurred. For this reason, calling certain cement products “chemically bonded ceramics” is justified. We will use the term chemically bonded ceramics or cements as

simply CBCs to address products containing crystalline as well as noncrystalline phases that are formed at room or near room temperatures.

Major research in CBCs has occurred in the last fifty years. Three significant product lines have been developed: alkali-activated cements, geopolymers consisting of aluminosilicates, and chemically bonded phosphate ceramics (CBPCs). Four books, namely, *Alkali-Activated Cements* by Shi et al. [5], *Geopolymers* by Davidovits [6] and also by Provis and van Deventer [7], and *Chemically Bonded Phosphate Ceramics* by Wagh [8], are comprehensive monographs on CBCs.

The first literature review on CBPCs was conducted by Westman [9], which spanned the years from 1918 to 1973. This was followed by Kanazawa [10], who presented a review of the literature from 1974 to 1987. Then came the emphasis of using CBPC dental cements, which led to an extensive overview by Wilson and Nicholson in their book [4]. Because of the rich literature and commercial applications of CBPC-based dental cements, particularly on zinc phosphate cements, it was believed that CBPCs were applicable to only phosphate dental cements and they could be produced only at small scale [11–19]. This picture changed after it was understood that the CBPCs can have far reaching applications, well beyond dental cements, into areas of nuclear sciences such as shielding of neutrons and immobilizing highly radioactive fission products, to products as common as construction cements and corrosion and fire protection coatings. This review traces these developments that occurred during the last twenty years with an emphasis on the progress of the last ten years.

Among these are the distinct CBC products, alkali-activated cements, that include Portland cement and geopolymers produced with alkaline materials. Both form alkaline cements or ceramics as the end product. On the other hand, the acid-base reaction concept described in Wilson and Nicholson's book [4] presents a unique way of synthesizing CBCs by reacting acidic and alkaline components. The authors describe a wide range of such CBCs, which include, phosphate-based CBCs (CBPCs), polyalkenoate cements, and oxy-chloride and oxy-sulfate cements. The subject of this paper is CBPCs. Wagh and his coworkers studied the chemical reactions between phosphoric acid or acid phosphates and various oxides that produce CBPCs, used solution chemistry and thermodynamics for clues to their syntheses, and produced magnesium phosphate [20], aluminum phosphate [21], and iron phosphate [22] ceramics. A comprehensive theoretical model that forms the basis of CBPC synthesis may be found in [8]. They also showed that variety of phosphate-based dental cements [4, 23–25] can be explained using their model. Based on their work, several commercial products have appeared in the market. This article reviews this recent advancement in CBPC products.

Though solution chemistry and thermodynamics provide clue to chemical synthesis of CBPC materials, products development needs much more than that. To produce commercially viable products, concepts of materials science and engineering are indispensable. Acid-base reactions can produce precipitates, but to produce ceramics or cements with

coherent bonding between the particles, certain conditions need to be fulfilled by the reaction product. For example, to form a crystalline structure, the molecules have to bond with Van der Waal, ionic, or covalent bonds in a short-range order but glassy phase may be produced with a long-range order as in polymers. In practice, there is little control over these and most CBPCs contain either crystals or glassy structure or both. Formation of coherent bonds is not instantaneous, which means the reaction should be slowed down and controlled to produce solid products. This requirement puts conditions on the rate of reaction. The product formed may be as small as few grams (as in dental cement) or as large as a monolith of 55 gal drum scale (as in Portland cement concrete). Production of large-scale objects by learning how small-scale dental cements are produced is a major challenge in CBCs and has hardly been addressed in the literature. For this reason, materials aspects of scaling of the products are very important, especially while developing commercial products.

Focus of the earlier literature on CBPCs has been on the basic chemistry, selection of suitable components for reactions that form ceramics, and laboratory scale proof of their applicability [8]. During the last ten years, however, efforts have been invested to take the technology to commercial scale. As a result of these efforts, few products are now marketed in nuclear and civil engineering applications, and more are being pursued. To develop user-friendly products, the processes have been modified and large-scale demonstrations have been held even for highly radioactive waste materials. The scale of the technology in these applications is not obvious. Due to the efforts in producing commercial products, the CBPC technology has become rugged and reproducible, applicable in different environment, less prone to human errors, and compliant with standards that are recommended for production processes and products. Focus of this article is on these aspects.

For clarity in the foregoing discussion, we need to address how we have used the words cement and ceramics. We will use the word ceramics, where we emphasize the crystalline structure, and cement to emphasize their application as cement (produced by large-scale pumping and pouring). Thus, the context will justify the nomenclature.

Finally, we would also like to emphasize that CBPCs can be used as coatings with either crystalline or noncrystalline structure. Thin coatings, being two-dimensional in geometry as against three-dimensional ceramics and cements, cannot be categorized either as ceramics or cements, and hence they need to be addressed as simply coatings or paints. Being two-dimensional, requirements on their structure, production, application, and performance are quite different from cements and ceramics. Therefore, we will treat coatings as a separate category in our discussion.

## 2. Role of Solution Chemistry and Thermodynamics in Formation of CBPCs

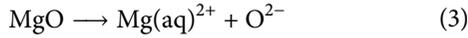
Aqueous solution chemistry is the key to fabrication of CBPCs. The phosphate component is an acid phosphate, and

the alkaline component is a sparsely soluble oxide or an oxide mineral. The acid phosphate releases phosphate anions in aqueous solutions upon its dissolution and lowers the pH of water. This increases the solubility of the sparsely soluble alkaline component and dissolves a small part of it into the acid solution. The reaction of the alkaline cation with the phosphate anion results in formation of the neutral phosphate that is the basic building block of the ceramic.

As examples of this process, consider dissolution of sodium and potassium dihydrogen phosphates ( $\text{NaH}_2\text{PO}_4$  and  $\text{KH}_2\text{PO}_4$ , resp.).  $\text{NaH}_2\text{PO}_4$  is completely soluble, while  $\text{KH}_2\text{PO}_4$  has a saturation concentration of only 20 wt.%. Release of acid phosphate anions in the solution is given by the following reactions

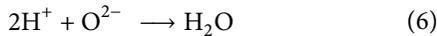
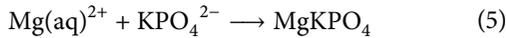
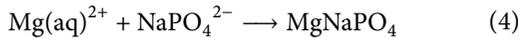


Release of hydrogen ions ( $\text{H}^+$ ) facilitates dissociation of the oxide. For example, if  $\text{MgO}$  is mixed with the above solutions, small part of it will dissociate according to

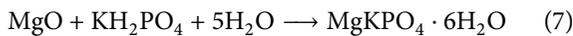


The (aq) sign with Mg ion indicates that it is an aqueous ion. Once it is ionized, due to charge screening by the polar molecules of water, there is a local rearrangement of atoms and molecules, and the thermodynamic properties of the aqueous ion would differ from that of nonaqueous ions of Mg. This effect has almost no bearing on our formation of CBPCs, except that we now need to consider the properties of aqueous ions in all our thermodynamic calculations, hence is the symbol (aq).

The cations and anions in the solution neutralize each other to form new compounds as per



Water that is produced and some of the free water from the solution end up as the water of crystallization (bound water) and the reaction products form crystals that can grow into insoluble solids, which form the chemically bonded phosphate ceramics. Equation (7) below gives the most common such ceramic, and products that utilize this binding system are called Ceramicrete [26]. The complete equation that forms this ceramic is given by



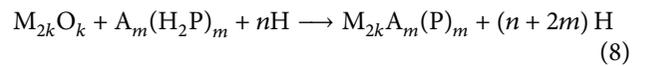
Using this concept of acid dissolution of sparsely (slightly) soluble oxides, it is possible to produce range of ceramics. Details of this concept and methods of exploiting the solubility of sparsely soluble oxides are described by Wagh and Jeong [8, 20].

In mineralogy,  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  was a less known mineral. However, it is equivalent to struvite,  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ,

that has been well studied (see sources such as Webmineral or Wikipedia). Recently, Postl et al. [27] and Graeser et al. [28] recognized this equivalence and studied the product,  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ , in detail. It has an orthorhombic colorless structure and now is known in mineralogical literature as K-struvite. Presence of K-struvite makes Ceramicrete highly crystalline as compared to Portland cement. This example indicates that CBPCs are ceramics rather than cements, though their fabrication mimics cements.

To produce CBPCs, the oxide component should be sparsely soluble. Often the solubility of the oxide, such as  $\text{CaO}$ , is too high to be exploited in the acid-base synthesis of CBPC formation. Very small sizes as that of dental cements may be produced but large sizes are virtually impossible. For this reason, it has not been possible to produce a calcium-based ceramic in a large size. In such cases, one needs to resort to use of a sparsely soluble compound of that oxide that may give the slow cation release rate needed to form ceramic. For example, Wagh and his coworkers produced ceramic using calcium silicate ( $\text{CaSiO}_3$ ) instead of  $\text{CaO}$  [29]. If the solubility of the oxide is too low, then other alternative methods to enhance the solubility are employed. Wagh and his coworkers raised the temperature of the solution to enhance the solubility sufficiently to produce ceramics of aluminum phosphate [21], and they also used reduction mechanisms to lower the oxidation state and then initiate the acid-base reaction to produce ceramics of iron oxide ( $\text{Fe}_2\text{O}_3$ , or hematite) [22]. They selected these oxides because of their abundance in nature. In practice, it should be possible to produce ceramics of many other oxides that are sparsely soluble.

There are three parameters that are key to determining the correct oxide or oxide mineral, which would form CBPC and physical conditions needed to form them. To discuss these, let us write a general acid-base reaction that forms ceramics using cement chemistry notation:



The terminology used in (8) is as follows:  $\text{M}_{2k}$  = metal of valency  $2k$ ,  $\text{O}$  = oxygen,  $\text{A}_m$  = alkali or a divalent metal of valency  $m$ ,  $\text{P} = \text{PO}_4$ , and  $\text{H} = \text{H}_2\text{O}$ . When  $k = 1$ ,  $\text{M}$  will be a divalent metal such as Mg, Ca, or Zn. If  $k = 3/2$ ,  $\text{M}$  will be a trivalent metal such as Al or Fe. For  $m = 1$ ,  $\text{A}$  is an alkali metal such as Na or K, and when  $m = 2$ ,  $\text{A}$  may be Ca, Mg, and so forth. Thus, using  $k = 1$  and  $\text{M} = \text{Mg}$ , and  $m = 1$  and  $\text{A} = 2$ , we can reproduce (7). The only difference is that the last term of water has become bound water in (7). In most reactions, part of the last term in (8) becomes bound water and the rest may remain as free water, which evaporates with heat generated during the reaction.

Solubility of sparsely soluble oxides is related to the basic thermodynamic property of Gibb's free energy of formation ( $\Delta G$ ) of that oxide and the absolute scale temperature  $T$ . Thus, it is possible to determine the solubility of these oxides by knowing their Gibb's free energy and also the pH of the solution. We will not go into detail about the theory behind it, but Pourbaix's book [30] is the best reference for this and

has all the information needed on solubility characteristics of oxides to find the right conditions to produce CBPCs.

There has been significant research in the kinetics of formation of CBPCs. Soudee and Pera [31, 32] studied the acid-base reactions in more detail and also established the importance of the surface area of magnesium oxide during the reaction. Similarly Carvalho and Segadães [33] studied the powder characteristics on the reaction kinetics. The physicochemical basis for the novel binders has also been provided by [34]. These investigations have established that the larger is the ratio of surface area to volume of magnesium oxide, the more rapid is the reaction. Alternatively, the smaller the magnesium oxide particles for the same amount of magnesium oxide are, the faster is the reaction.

Chinese research [35, 36], on the other hand, focused on kinetics of reaction and setting characteristics of K-struvite based CBPCs. They confirmed the findings of Wagh's group [20] that the oxide component in K-struvite based CBPC does not react completely and some magnesium oxide remains as an inert filler. This filler has an advantage. It acts as an obstacle to crack propagation in the ceramic and thereby enhances the strength properties of the ceramic. Therefore, one may conclude that Ceramicrete is a composite of K-struvite and magnesium oxide.

Wagh [8], and Wagh and Jeong [20] and coworkers have provided details of the thermodynamic basis of solubility of sparsely soluble oxides and identification of candidate oxides to form ceramics and hence we will not go into detail about that. It suffices to say that this theory helps one to identify which oxides are suitable for formation of ceramics and which need additional treatment of to form ceramics.

The second thermodynamic parameter that is important is the enthalpy of formation. Enthalpy difference between the end products and reacting components gives us heat output during the acid-base reaction. Estimation of heat generated during ceramics synthesis is very important because excessive heat may boil water in which the acid phosphate is dissolved. At the same time, if the heat output is too small, ceramics formation will take a long time. Production of heat is also directly proportional to the size of the sample and hence producing larger batches of ceramics is very difficult, unless the rate of production of this heat is controlled. In recent years methods have been developed to control this heat either with chemical retardants or by using pumping methods that lend themselves to mixing of smaller volumes continuously and building up ceramic volumes. Thus the thermodynamic basis leads one to predict how one can use oxides and minerals available in nature to produce CBPCs of desired compositions. This is discussed in the next section.

### 3. Generalization of CBPC Syntheses

Based on the thermodynamic analysis and using the condition that the metal oxide should be sparsely soluble, one can select oxides that are most suitable for forming ceramics. Generally divalent oxides are the most suitable for forming ceramics. Certain trivalent oxides, such as lanthanide oxides, also can be used to form ceramics. However, when the solubility is lower, other methods of enhancing solubility

are used. Iron oxides provide a good example of this. Fe is both di- and trivalent and its corresponding oxides are FeO (wustite) and Fe<sub>2</sub>O<sub>3</sub> (hematite). FeO can be reacted with either phosphoric acid solution or a solution of an alkali metal phosphate to form ceramic, but Fe<sub>2</sub>O<sub>3</sub> does not react with any phosphate solution. However, Wagh and his coworkers have demonstrated that Fe<sub>2</sub>O<sub>3</sub> can be slightly reduced using elemental iron in a small quantity and they formed ceramic of iron phosphate [22, 37]. In addition, they showed that magnetite, Fe<sub>3</sub>O<sub>4</sub>, when reacted with phosphoric acid solution forms ceramics, and the process does not need any reduction. This is understandable as Fe in magnetite is in a slightly lower oxidation state of Fe<sup>+2.67</sup> as compared to Fe in Fe<sub>2</sub>O<sub>3</sub>, which is in a higher oxidation state of 3+.

The ability to produce a very wide range of CBPCs using oxides or minerals of range of elements makes CBPC process far more general. Therefore, it should make a great impact in various industrial and environmental applications. The length and breadth of applicability of these materials are discussed in Section 3.1.

*3.1. Elements of Current Interest in CBPC Formation and Applications.* A literature review indicates that CBPCs have been developed and initial demonstrations have been conducted in the following fields:

- (1) immobilization of radioactive waste and mixed waste streams,
- (2) nuclear shielding materials,
- (3) corrosion and fire protection industrial coatings,
- (4) structural products,
- (5) dental and prosthetic cements.

To understand how CBPCs could be useful in such wide-ranging applications and to identify potential compositions in each case, some guiding principles must be set forth using the solubility product constants of individual oxides.

To identify the role of potential metal oxides as candidates for forming CBPCs, the following guidelines may be used.

*3.1.1. Alkali Metal Oxides.* Alkali metal oxides are readily soluble and as a result release cations too rapidly; hence they are not suitable to form CBPCs. The only way they can be used as acid phosphates such as NaH<sub>2</sub>PO<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub>, or CsH<sub>2</sub>PO<sub>4</sub>. Sodium, being very leachable element, NaH<sub>2</sub>PO<sub>4</sub>, is not used commonly in CBPCs. The most common acid phosphate used is KH<sub>2</sub>PO<sub>4</sub> and is probably the only acid phosphate currently used in most applications, though it is possible to use acid phosphates of divalent metal oxides also as we shall see in Section 3.1.2. Acid phosphate of Cs is very expensive and hence is not suitable for cost effective applications. However, Cs has a radioactive isotope Cs-137 that is formed in nuclear reactions. As a result, CsH<sub>2</sub>PO<sub>4</sub> provides a pathway to immobilize this fission product and hence is of very much interest in CBPC applications in nuclear industry.

**3.1.2. Divalent Metal Oxides.** They are the best candidates to form CBPCs because of their sparsely soluble nature [8]. They are used as the alkaline components in the acid-base reaction. As mentioned before, CaO has very high exothermic reaction with an acid phosphate and it is very difficult to produce ceramic using this oxide. One way to get around this problem is to use minerals of Ca that release Ca very slowly in the solution (sparsely soluble minerals). Such compounds of Ca have been used in dental cements [38]. As mentioned before, Wagh et al. [29] also developed CBPC using wollastonite ( $\text{CaSiO}_3$ ), which is a low-cost mineral. They studied the solubility of this mineral as a function of pH and found that the solubility product is in the correct range. This helped them to produce its ceramic. An overview on calcium phosphate cements may be found in the article by Chow [38].

Similar is the case with ZnO. Due to high exothermic heat release during the acid-base reaction, ZnO is not a good candidate for producing large-scale CBPCs. High cost of ZnO is also an issue. However, early commercial dental cements, in which neither cost nor the size were issues, were produced using ZnO and did well in the market [3].

MgO is the most common oxide that is used to produce practical CBPCs. As is, its solubility is high and it releases large amount of heat. However, dead burnt MgO (calcined to very high temperature) has a crystalline phase called periclase [39], which is the most suitable phase of this oxide to produce CBPCs. Range of CBPCs, such as those produced from the reaction with ammonium phosphate [40, 41], aluminum dihydrogen phosphate [42], magnesium dihydrogen phosphate [43], and potassium dihydrogen phosphate [9], were all produced using dead burnt MgO. These demonstrations indicate that periclase also enables one to produce CBPCs by reacting with divalent and even some trivalent metal acid phosphates (such as that of Mg, Ca, Al, etc.). This widens the range of CBPC products. Among these only potassium dihydrogen phosphate (Ceramicrete) has been the most successful commercial product and has not exhausted the range of its applications, implying divalent and trivalent metal acid phosphates will have to wait for their opportunity to find applications.

Other oxides that fall in this category are FeO (wustite), CrO, MnO, CoO, and so forth. They are not abundant in nature and hence are not economical for production of useful CBPCs. However, their role in immobilization of waste is still important especially with hazardous metals such as Cr, which we will see below.

**3.1.3. Trivalent Metal Oxide.** The trivalent metal oxides, such as  $\text{Fe}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$  (and other members of lanthanide group in trivalent state),  $\text{Al}_2\text{O}_3$ , and  $\text{Bi}_2\text{O}_3$ , have solubility lower than that of divalent metal oxides. Unpublished work by Wagh has shown that oxides of La, Ce in trivalent state, and Bi can still be used to react with phosphoric acid solution to form CBPCs.  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  have very poor solubility and hence it has not been possible to produce CBPCs using them at least at room temperature. To produce CBPCs, Wagh and his group enhanced the solubility by using a reduction method of adding a small amount of Fe in  $\text{Fe}_2\text{O}_3$  and phosphoric acid solution mixture [22] and produced iron phosphate CBPC.

They also conducted the acid-base reaction of  $\text{Al}_2\text{O}_3$  and phosphoric acid solution at about  $150^\circ\text{C}$  [21] and produced aluminum phosphate CBPC. These methods are inexpensive and produce ceramics at lower temperatures compared to sintered ceramics.

$\text{Fe}_3\text{O}_4$  (magnetite) is an interesting oxide. It may be considered as a combination of FeO and  $\text{Fe}_2\text{O}_3$ . Presence of FeO makes it suitable for forming CBPC matrix. Wagh and his group demonstrated this by reacting it with phosphoric acid solution [22]. Similar should be the case with  $\text{Mn}_3\text{O}_4$  as its solubility is similar to that of  $\text{Fe}_3\text{O}_4$ .

**3.1.4. Oxides of Metals of Higher Valency (Except Zr of Valency +4).** Metals of valency  $>3$  are of little interest in forming CBPCs because of their extremely low solubility. Exception is that of  $\text{ZrO}_2$ , which is sparsely soluble in acidic region and forms  $\text{ZrOOH}$ , which then reacts with an acid phosphate and forms ceramic. Singh et al. [44] have succeeded in producing ceramics of this oxide.

**3.1.5. Oxides of Radioactive Elements.** Elements such as uranium (U), thorium (Th), and plutonium (Pu) are constituents of radioactive waste that has resulted from development of nuclear weapons and are also major parts of spent nuclear fuel [45–51] stored in water pools near the nuclear reactors. Significant radioactive waste is also generated in power plants by contaminated equipment, gloves, and other safety wear. These elements need to be immobilized so that they do not enter the ecosystem through groundwater or air. In fully oxidized state, they are insoluble in water and hence do not form phosphates. However, for the same reason, if they are microencapsulated in the CBPC matrix, they are isolated from the environment and hence have no opportunity to get into groundwater. All earlier research in immobilizing elements of lower oxidation states has shown that they oxidize in the phosphate matrix and reach into full oxidation state. Reader is referred to Chapter 17 of [8] for details.

**3.1.6. Major Fission Products [52, 53].** With the exception of technetium (Tc), fission products are natural elements and their isotopes are also produced in a nuclear reaction. Tc, on the other hand, is produced only in nuclear fission.

Fission products are comparatively short lived (several tens of years) but their activity is extremely high. Even when this activity is depleted severalfold, it is still radioactive. Therefore these isotopes need to be immobilized for safe storage. CBPC approach is the most ideal for these. Details are discussed later in this paper.

**3.1.7. Hazardous Elements.** Resource Recovery and Conservation Act (RCRA) of US Environmental Protection Agency [54] has identified arsenic (As), chromium (Cr), cadmium (Cd), nickel (Ni), mercury (Hg), lead (Pb), silver (Ag), selenium (Se), and barium (Ba) as elements potentially hazardous to human health if consumed via food, water, or air. Among these, zinc (Zn) is a borderline element that may be regulated in future under RCRA, but we have included it in our discussion as the CBPC technology has potential to stabilize it very effectively.

### 3.1.8. Benign Elements That Simulate Radioactive Elements.

It is difficult and expensive to handle radioactive isotopes in exploratory immobilization experiments because of their radioactivity and associated safety measures needed to handle them. Also such experiments generate their own waste, and if initial experiments are carried out with actual waste streams, they only add to the existing radioactive waste. For this reason, their chemically equivalent metals that are nonradioactive are used in initial immobilization studies. These equivalent metals are termed as simulants or surrogates. Based on the chemical behavior (such as reactivity, solubility, etc.), uranium, thorium, and other transuranics are substituted by Ce. Neodymium represents radioactive Americium. Fission products such as Cs-137, Sr-90, and I-131 are substituted by their nonradioactive counterparts Cs, Sr, and I. Since Tc-99 is formed only in nuclear reaction, it does not have its nonradioactive counterpart, and hence rhenium is used as its simulant.

While developing CBPCs for immobilization of radioactive contaminants, these elements are used to simulate radioactive isotopes, the processes are optimized, and then only the actual radioactive isotopes are introduced for the final demonstration. This helps in reducing the cost of development of immobilization technologies. It also reduces the additional radioactive waste that would have been generated during research and development.

**3.2. Binders and Fillers.** Zinc phosphate dental cements were produced by reacting zinc oxide with phosphoric acid solution [24]. As mentioned before, due to the high exothermic heat output, the product could be made in a small scale (in few grams) only, and it was virtually impossible to mix large quantity of this material to form big shapes. Therefore, its application of zinc based CBPCs is limited to dental cements.

Subsequent studies by Sugama and Kukacka [40, 41] addressed this problem by using ammonium acid phosphates for reaction with magnesium oxide. Their approach included the following major improvements.

- (1) Increasing the pH of the acid: they used either mono- or diammonium phosphate (fertilizer components) instead of phosphoric acid and raised the pH of the acid component. This reduced the pH difference between the acid and the alkaline oxides and that slowed down the reaction slightly.
- (2) They also replaced zinc with calcined MgO, which has a much lower solubility in the acidic solution. Slower dissolution led to slower reaction.

This approach of using an acid phosphate instead of phosphoric acid solution, and use of calcined MgO, paved the way for more practical CBPCs [55–57]. Using Sugama's approach, few gallons of the product could be produced at a time that would give work time of about 15–20 min. At least one product, Set 45, found market [58] as a road repair material. More importantly, however, it paved the way for further research at Argonne National Laboratory geared towards practical CBPCs. Wagh and his coworkers used monopotassium phosphate instead of ammonia-releasing

TABLE 1: Density, porosity, and compressive strength of CBPC with fly ash as an extender [26].

Sample description	Density (g/cm <sup>3</sup> )	Connected porosity (vol. %)	Compression strength (psi)
Phosphate binder	1.73	15	3,500
Class F loading (wt.%)			
30	1.67	5.22	5,651
40	1.77	4.09	6,207
50	1.8	2.31	7,503
60	1.63	8.15	5,020
Class C loading (wt.%)			
30	1.97	4.79	8,809
40	2.07	3.4	11,924
50	2.06	5.34	7,608
60	1.92	8.02	4,753

ammonium phosphate products [4, 20]. There have been few other similar attempts by other researchers to develop sustainable products such as cement mortar using the CBPC concept [59]. This led practical CBPCs that were developed for immobilization of radioactive waste streams [60] initially but also found market subsequently in structural and architectural market.

Despite these advances, one could not develop low-cost processes for production of CBPCs as engineering materials for range of structural materials applications. When produced in a large volume (like in several cubic meters) CBPCs still produced large amount of heat. As done in Portland cement concrete, incorporating fillers and extenders was considered as a solution. This approach has threefold advantage. For a given volume, the amount of binder used is small and hence less heat is generated. This extends the working time. Presence of fillers increases the heat capacity of the mixture (especially if one uses aggregates such as sand, pea gravel, and stones), which in turn lowers the temperature rise of the CBPC product during its formation and slows down the setting process and gives more working time. Finally, due to smaller amount of the expensive binder in the product, the products are cheaper.

Wagh and his coworkers also [26] found an additional advantage. Use of fly ash from coal burning utility plants increased the compressive strength of the product two-to threefold (see Table 1). The dramatic increase in compressive strength is likely to be a result of additional reactions between the acidic phosphates and amorphous silica from ash. Wilson and his coworkers have studied the role of soluble silica in forming dental cements [61], and we feel reactions similar to what these authors found are responsible for enhancement of the strength properties. Detailed fundamental studies are needed in this area, because analytical techniques for reactions with amorphous products have limitations. Even X-ray diffraction technique used for crystal detection cannot be used in such cases.

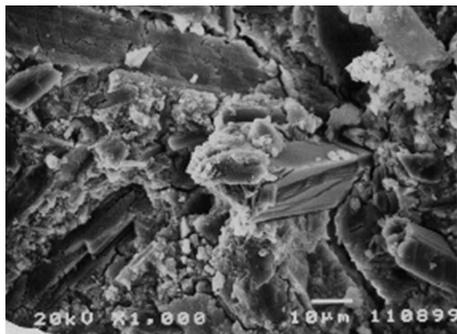


FIGURE 1: Scanning electron micrograph of magnesium potassium phosphate CBPC and wollastonite composite. One may see the elongated grains of wollastonite embedded in the CBPC matrix [29].

In another study [29], Wagh and his coworkers also looked into adding calcium silicate (wollastonite,  $\text{CaSiO}_3$ ) as filler. The advantage of this mineral is that its grains have acicular structure (elongated) as may be seen in Figure 1. The result is, enhanced flexural strength of the product.

If one could add whiskers to the CBPC matrix, the flexural and tensile strength can be enhanced. Wagh and his coworkers tested addition of chopped glass fibers of 0.25 and 0.5 inch fibers at a loading of 1–3% and demonstrated that the flexural strength of CBPC ash composite can be increased from 900 psi to double its value [8].

One may also use CBPC as an adhesive on natural fibers to produce fiberboards and other articles. Latitude 18, Inc., took up these ideas. Patent granted to Wilson et al. [68] goes well beyond whiskers and suggests compositions for fiberboards and even phosphate bonded cellulosic paper. These developments are still in their infantile stage and several technical hurdles such as miscibility of the fibers and whiskers in phosphate binders during production, pumping, and so forth need to be resolved before one can talk about the products.

#### 4. Products and Applications

In an endeavor to produce marketable products from the laboratory results for any material several major milestones are involved, which include testing of all useful properties, optimization, then scaling up the production process, finding suitable equipment to deliver the product for individual applications, and finally selling the products in the market.

CBPCs have gone through these stages in the past 20 years. In the process, several products have found market in a small scale, and several are just being launched in a big way. The smaller scale applications have been documented in the literature and commercial websites. These include Monopatch (<http://www.bindancorp.com>) and Grancrete (<http://www.Grancrete.net>). Some of the larger scale applications have been in nuclear waste immobilization and shielding applications and development of products for fire and corrosion protection. This section provides an account of investigations behind these products and their performance and methods of applying them.



FIGURE 2: Drum scale immobilization of contaminated soil (courtesy: Argonne National Laboratory).

**4.1. Application Methods.** Unlike Portland cement, CBPCs are rapid-setting materials. The acid-base reaction that produces them may be slowed down using retarders, such as boric acid or other boron products.

Even with the best efforts, setting of the product can be delayed by approximately half hour. This gives a maximum of 45 min to workers to mix the ingredients, fillers, and water and produce paste and deliver it through suitable pumps. When the product sets, however, it is almost a flash set. Continuous use of equipment for mass production also heats the equipment and subsequently reduces the time of setting. Though half an hour to 45 min is a reasonable duration, it is still not practical for many operations. Therefore, engineers have spent significant time to overcome these difficulties and developed processes for individual applications.

These delivery processes fall in two categories. The first one is a batch process. It is applicable for small volume applications, such as hazardous and radioactive waste immobilization in low volume, dental, and prosthetic cements, and repair applications such as filling potholes and driveway repair. In this method, all ingredients and water are added in a container and mixed with a paddle and the paste is poured or pumped within a short time or applied by hand.

Figures 2 and 3 show use of this method for radioactive or hazardous waste immobilization and as road surfacing material. In Figure 2, a vertical mixer (shown in the background) is used, which has a paddle that can be inserted in the drum. The paste is mixed in the same drum that is used for storage of the immobilized waste in a repository. In Figure 3, a conventional concrete mixer is used to produce paste that is poured and leveled.

The second category is designed as a continuous process. Large volume mixing of waste and binders and then pouring in containers or pits for storage, or corrosion and fire protection coatings, insulation grouts, and so forth fall in this category. Typically a plural delivery system is used for these applications, in which the acid slurry is delivered from one line and alkaline from the other. Both are pumped continuously to a single mixer, which mixes the two components in



FIGURE 3: Repair of Pennsylvania Turnpike using CBPC-based Monopatch (courtesy: Bindan Corporation, USA).

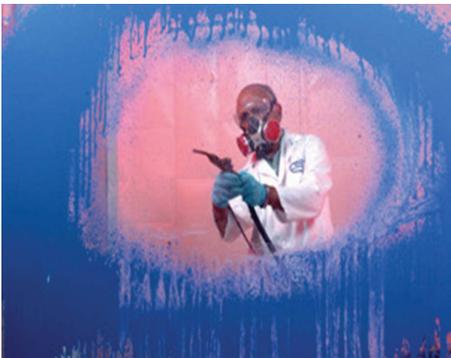


FIGURE 4: CBPC coatings spray demonstration with a spray gun (courtesy: Argonne National Laboratory).

a small quantity at a time and delivers it continuously from a nozzle for the desired application. For thin coatings, a spray gun is mounted at the end, which sprays it on any vertical wall or on horizontal floor. Figure 4 shows the demonstration of producing thin coating films of 150–250 micrometer thick.

The batch mixing process is similar to mixing concrete. The continuous mixing and pumping of individual components and then pouring are done in polymer industries and spraying is used in paint industry for emulsions. Rarely paste formed by a mixture of particulate and water is used in the paint industry and hence adapting to the pumping methods for CBPC paints and coatings is not obvious, because CBPC pastes are always aqueous particulate mixtures. Since a pumping operation is largely dependent on rheology of the paste, a delivery system for CBPC pastes requires more than routine knowledge of pumps. In particular, MgO powders are not one of the friendliest ones when it comes to pumping in slurry form. Once pumped, however, the mixed paste can be sprayed as a thin coating approximately 125  $\mu\text{m}$  thick or same as that of commercial paint or as thick as commercial grouts.

*4.2. Research and Development in Nuclear Shielding Applications and Products.* Nuclear radiation consists of alpha, beta,

gamma rays, and, in addition, neutrons. Alpha rays consist of helium nuclei, which are heavy enough to be absorbed easily by solid materials and hence any solid or liquid material of small thickness on their way can shield them. Beta radiation consists of electrons and positrons and is again stopped by few millimeters thick materials such as aluminum. Therefore, the major issue is that of gamma rays and neutrons that are very highly energetic radiations and also penetrate materials used in nuclear reactor vessels (concrete and steel).

The problem is not limited only to active nuclear power plants. Interim storage of nuclear fuel, spent fuel rods that are replaced by new rods in a power reactor, storage of excess high energy nuclear materials such as highly enriched uranium (HEU) produced during cold war era that remained unused [69] all require shielding materials to store them so that their radiation is not released in the neighboring environment. Even nuclear waste that resulted from development of nuclear arsenal during the Second World War and cold war needs secure storage facilities in the United States and Former Soviet Union countries. Needless to say that good shielding materials are needed in the nuclear disaster areas such as Chernobyl [45] and Fukushima [46] for containment.

Denser materials or products made from heavier nuclei are the best candidates for shielding gamma rays. Common steel is a cheap gamma ray shielding material because iron is dense. Therefore steel is a preferred metal to manufacture reactor vessels.

Neutrons, on the other hand, have exactly opposite characteristics. They are absorbed by light nuclei and penetrate through heavier metals. Any hydrogen-containing materials, and low atomic weight elements in the periodic table such as carbon and boron, are the best performing candidates. Water is ideal. Therefore, spent fuel rods, once they come out of the reactor, are stored for several years in water pools for cooling (note that the first event that occurred in Fukushima was a breach in such a pool, where leak occurred and water drained exposing fuel rods to meltdown [46]). Thus a paradoxical situation arises while choosing materials: the one good for gamma ray shielding is not suitable for neutrons and vice versa.

The best compromise is to use steel for gamma rays and concrete barrier for neutrons. Concrete contains sufficient water and hence hydrogen. It is made of lower atomic weight materials such as Ca, Si, and Al. For this reason, concrete barriers are commonly used for shielding of neutrons. The problem with concrete, however, is that large thickness is needed for sufficient shielding. While it may work in a power plant where thick walls can be built, it is not a suitable material if nuclear material needs to be transported, or temporarily stored because of its weight and volume.

For example, once the rods cool down (or their radiation decreases to sufficiently low level), they still need to be transported in shielding casks and stored permanently in repositories. These casks need to be light, which makes thick walls of concrete unacceptable. They need to resist impact, heat, freeze-thaw conditions, and corrosion. High impact strength is difficult to achieve with concrete.

CBPCs have been evaluated as shielding materials for neutrons, because of their lighter weight and their ability

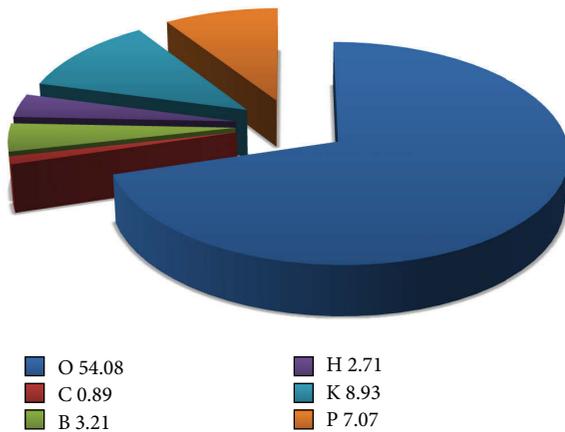


FIGURE 5: Composition of CBPC nuclear shield for neutrons [71].

to incorporate higher level of boron. Work done in a joint program between Argonne National Laboratory of the US Department of Energy, Russian Federal Nuclear Center in Sarov, Russia, and Eagle Picher Industries in the US [70, 71] showed that significant amount of boron carbide can be incorporated in CBPC. Joint efforts between these organizations came up with an optimal formulation to efficiently shield neutron radiation. A typical composition of CBPC proposed by this work is given in Figure 5.

Following this study, Eagle Picher Industries finalized a composition for a material called Borobond. They worked with Oak Ridge National Laboratory (ORNL) and developed Rackable Can Storage Boxes (RCSB) for safe storage of HEU. ORNL conducted modeling and experimental studies of such boxes with fixed natural  $B_4C$  and water content [72]. Their study led to a method of quantifying the water content of RCSBs by fast neutron time-of-flight transmission measurements (NMIS) and  $B_4C$  content with gamma ray spectrometry for known water content. The time-of-flight transmission measurements used in their investigations can also be used to assess the uniformity of Borobond in the RCSB. Their methods are tools at the RCSB production and at storage site during the operating lifetime of the RCSBs for storage of HEU.

Figure 6 shows how neutron shielding is dependent on water content and boron carbide concentration in Borobond. The density of the recommended product was  $1.9 \text{ g/cm}^3$ , less than that of concrete, and yet it has superior mechanical properties as shown previously in Table 1. It has all light elements and boron carbide content is as much as 4.1 wt.%.

This composition was used by Eagle Picher to produce RCSBs for DOE, which has stored HEU at one of its facilities. Currently Borobond is a product line of Ceradyne Corporation, a 3M Company.

Noting that spent nuclear fuel cannot be stored in water pools forever and must move into a dry storage facility, Argonne National Laboratory and Federal Russian Nuclear Center scientists continued their studies to evaluate feasibility

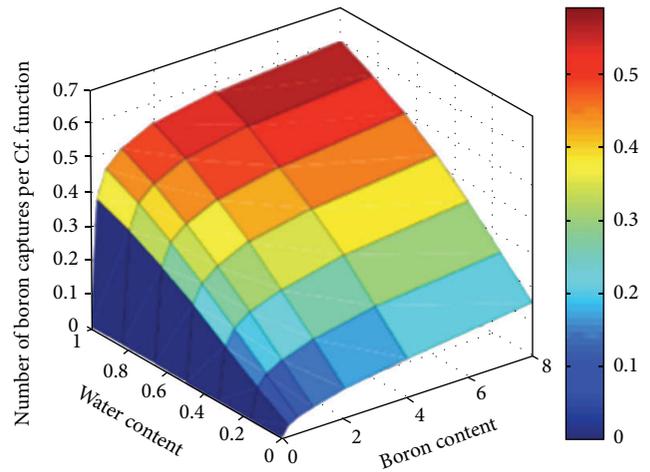


FIGURE 6: Calculated number of boron captures as a function of  $B_4C$  and content of water (wt.%) [72].

of using boron-containing CBPC (Ceramicrete in this case) for applications such as storage and transportation casks of nuclear materials. The work was computational. A Russian cask Model RT5010 [71] was used for this study. The design of the cask is shown schematically in Figure 7.

This study reached to several useful conclusions.

- (1) CBPC with boron carbide is very effective in thermal neutron capture. Thermal neutrons make up for the most flux of neutron radiation from the spent fuel that would be stored in a dry cask.
- (2) A boron carbide content of  $>5\%$  does not increase the shielding potential of the CBPC significantly thus 5 wt.% is practical.
- (3) If the temperature of the shielding layer is  $<100^\circ\text{C}$ , the bound water remains in the shielding layer and helps in shielding neutrons. At higher temperatures, the bound water is released; if it evaporates from the cask, the shielding property will be affected adversely. In practice, the shielding layer will be sealed and the evaporated water will remain as vapor and hence this will not pose a major issue in designing a cask.
- (4) Assuming the bound water remains within the shielding material, one can expect 50 to 80% shielding of neutron flux for the cask model shown in Figure 8.
- (5) Overall, for the design shown in Figure 7, boron-containing CBPC offers a better shielding option compared to others with boron and fillers.

Based on this study, further developments are underway between Argonne National Laboratory, American Industry, and Former Soviet countries for superior shielding applications of CBPC-based nuclear shielding products Figure 11.

*4.3. Recent Advances in the CBPC Technology for Nuclear Waste Immobilization.* Nuclear waste has its origins in development and production of nuclear weapons in the United States, Former Soviet Union, and to some extent in UK. These

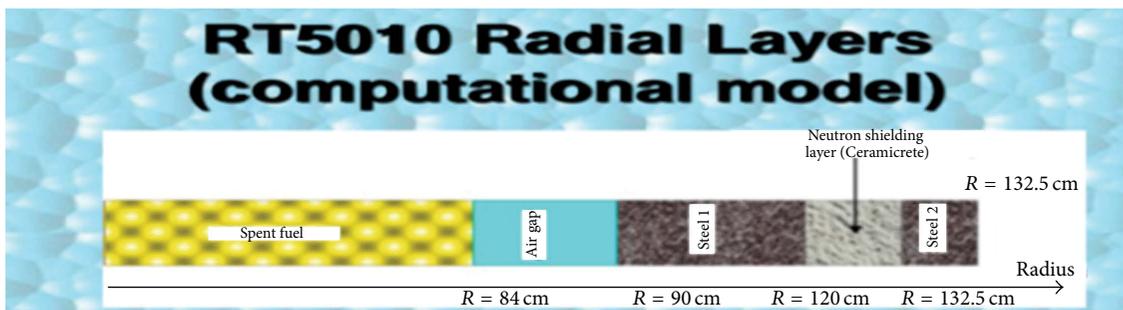


FIGURE 7: Cross-section of Russian dry storage cask Model no. RT 5010 used in the study of CBPC for neutron shielding in the Argonne-Russian Federal Nuclear Center study [71].

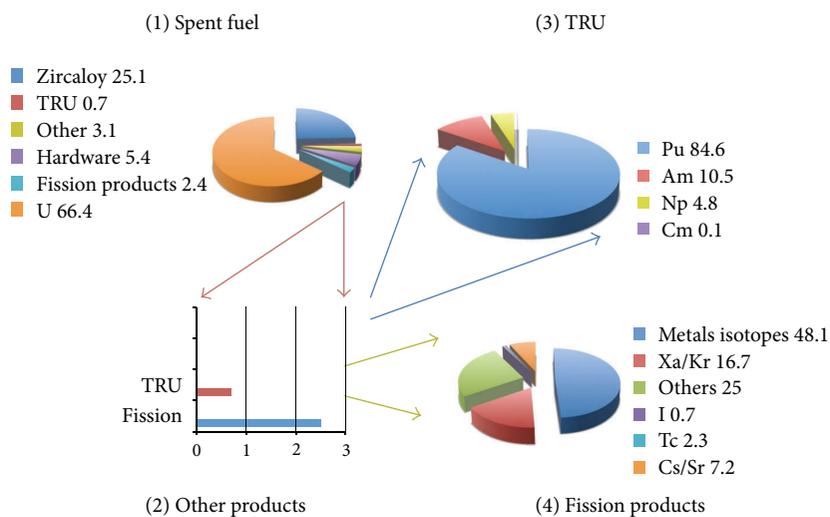


FIGURE 8: Typical mass composition of spent nuclear fuel [73].

countries have accumulated huge amount of nuclear waste in all forms, solids, sludge, and liquid [45]. The waste can be highly radioactive or may have very low activity. Due to the race between the western and eastern bloc countries to produce nuclear weapons, there was little regard for safe and long-term storage of such waste, but because of the current awareness of the consequences of various radioactive waste streams on the environment, habitat, and human health in both regions, efforts are being made to find ways to recycle or immobilize these waste streams for safe storage and to protect the environment.

The mankind has faced another acute problem of nuclear contamination of the environment resulting from the two major nuclear accidents (Chernobyl and Fukushima) in recent years. The clean-up efforts also have generated significant amount of waste that needs isolation [45, 46]. As a result, there is urgency in finding suitable materials to immobilize range of waste streams generated by such catastrophes.

Ceramicrete was developed to address these needs and much has been published in the earlier literature on this topic. Interested readers may find more details in the book by Wagh [8] and other articles [74, 75]. In the last decade, however, further advances have been made in this area.

**4.3.1. The Nuclear Legacy Waste Streams.** The major contaminants encountered during treating these waste streams are listed below.

- Hazardous inorganic contaminants: both high and low-level waste streams may contain these chemically hazardous contaminants. As listed in Section 3.1.7, Pb, Cd, Cr, Hg, and As are the elements of main concern in radioactive waste also. When both radioactive and hazardous contaminants exist in the waste, such waste is called mixed waste. Chemical immobilization of these elements, that is, converting them to insoluble compounds, is the best strategy to arrest leaching of these elements [76, 77], which is used extensively in the CBPC technology, because phosphate treatment employed in the CBPC technology results in insoluble phosphate salts of these elements.
- Actinides: actinides, especially Th, U, Pu, and Am, are prevalent in the waste, but also in spent fuel rods because they are the source materials for nuclear energy. They are mainly alpha and gamma emitting materials, and if active, they will also emit neutrons. They all have high atomic weight, their solubility is almost negligible, and hence they are not dispersible

in ground water. The only source of contamination of these materials is their dispersibility as solid fine particles, which can be arrested by microencapsulating them in the CBPC matrix.

- (c) Fission product isotopes (Cs-137 and 138, Sr-90, Tc-99, and I-131): these isotopes of cesium, strontium, technetium and iodine are formed during a nuclear reaction. Their relevant properties are listed in Table 3.

Since most of the work on low-level waste streams was reported in the earlier literature [74, 75], we will only discuss the extensive research done during the last ten years, which was focused on high-level waste streams. Among several options available for immobilization of these radioactive waste streams [78], the most preferred technology has been borosilicate glass technology [79, 80]. Waste and glass frits are mixed together and vitrified at temperatures ranging from 1200°C to 1500°C. This results in a homogenous glass waste form that has been shown to be stable for a time scale (million years) at which time the activity of the radioactive components is reduced sufficiently that it will not affect the environment. It can microencapsulate transuranics extremely well. However, this process is not suitable for high activity waste streams, because of the volatile components containing the fission products of cesium, strontium, technetium, and iodine (see, e.g., [81]). As one may notice from Figure 8, the amount of the fission product stream is small, just a fraction of a percent of the total waste. And yet, because of their high activity and their ability to become airborne during the vitrification process, they are unsuitable for vitrification process and hence are separated into high activity waste streams. As we shall see below, the CBPC process has been the most successful in mineralizing the fission products into stable phosphate compounds and hence immobilizing them.

The high activity tank waste streams have resulted from production of weapons grade nuclear fuels in the United States and Former Soviet Union countries. Most are stored in underground storage tanks in the US at Hanford tank farms in the State of Washington, Savannah River in South Carolina, and some in Idaho. The waste streams vary in their characteristics and composition but are either liquids or sludge. Reference [82] and references therein provide an overview of the tank waste streams within the US DOE complex and their characteristics.

While the bench scale testing was done in several earlier projects, full testing and large-scale immobilization experiments were conducted and success of the technology was demonstrated in collaborative projects between Argonne National Laboratory and Russian scientists on the two most difficult high activity tank waste streams [83, 84]. This work may make a major impact in the near future on immobilizing such waste streams with CBPC formulations.

The high activity in these waste streams arises from the fission products, prominently containing isotopes listed in Table 3. Also the waste streams can be acidic or alkaline depending on whether attempts were made to neutralize them with NaOH. Often neutralization results in alternative problem of immobilizing waste streams rich in leachable sodium Table 5. Thus the problem of immobilizing tank waste

streams boils down to the following three: (a) immobilizing fission products and trace levels of actinides, (b) getting rid of excess water without volatilizing any of the contaminants, and (c) immobilizing sodium to a level that it does not leach out sufficiently to affect the structure of the waste form.

Several studies have been conducted in demonstrating immobilization of these waste streams using CBPCs [85–88]. Notable and detailed analysis among these was done in a collaborative project between Argonne, Vernadsky Institute of Radiochemistry in Moscow, and Production Research at Mayak, a nuclear waste facility in Russian Federation, which also has stored similar waste Figure 10. Reference [64] provides the major results of the entire project. This project demonstrated immobilization of typical two high activity liquid waste streams from Hanford and two from Mayak. This team effort was highly successful in showing the simplicity and effectiveness of CBPC in immobilizing these waste streams at small scale to 55 gal drum size. Initial study was with simulated waste streams and success of this study led the scientists to tackle actual waste streams. Reference [88] contains details of the methodology, nature of the waste streams, additives in the CBPC formulations to immobilize difficult contaminants, properties of the waste forms, and their performance.

This collaborative work directed by Argonne National Laboratory on behalf of the US Department of Energy makes all other similar work outdated, because this work used the methods developed in previous work, tested, and then went beyond to produce waste forms at production level. The team concluded that CBPC technology can be used in practice without any concern about pyrophoricity, volatility, gas generation, or leaching of contaminants. For this reason, we will not delve on any other previous work but summarize results of this project.

Table 4 lists the composition of each of the waste stream.

Details of adding these stabilizers are described in the paper [88].

It is the opinion of this author that Cs and Sr do not need stabilizers, because using the solubility analysis presented in [8], it is possible to show that Sr is a sparsely soluble metal and it will form SrKPO<sub>4</sub>. Cs being an alkali metal will be converted to insoluble MgCsPO<sub>4</sub>. This mineralization of Sr and Cs has been verified in the author's unpublished work. Both SrKPO<sub>4</sub> and MgCsPO<sub>4</sub> have negligible aqueous solubility and, as will be seen later, perform well in leaching tests.

Table 6 lists the waste loading in the final waste forms and their physical properties. All results are reproduced from [88].

For waste streams with low-solid content of 16–52 wt.% solids, the waste loading has been very significant. This is because, as in Portland cement, CBPCs require water and bind significant amount in their crystalline structure.

There are both benefits and drawbacks of the approach of binding water and increasing the waste loading. For example, if glass vitrification technology is to be used for immobilizing these waste streams, the water will evaporate, but then the fission products will also evaporate causing

air contamination. They can be captured somehow in off-gas system but then need a lower temperature method of stabilizing them. At the same time, the vitrified waste form will have very small volume and will cost a lot less in transportation and long-term storage. On the other hand, the CBPC waste form provides a significantly simpler process with the least concern for volatility of the fission products but increases the cost of transportation and storage because of its large volume.

The effectiveness of waste immobilization method is determined by mainly three tests. American Nuclear Society's ANS 16.1 test [89] determines the leaching index (negative of logarithm of the diffusion constant) for each of the radioactive contaminants. The test is carried out at room temperature by immersing a geometrically regular sample in deionized and distilled water over 90 days. Aliquots of the leachate solution are drawn at specified periods and analyzed for the contaminant concentration. These numbers allow one to determine the diffusion constant of the particular contaminant in the waste form and that in turn allows one to represent the result as the leaching index. Table 7 summarizes these results in this project.

The other leaching test is for the durability of the waste form itself. Product Consistency Test (PCT) [66] determines the leaching rate of the major components of the waste form. The test was designed for vitrified glass and, hence, the components are Si, Ca, Al, and B. For CBPC, however, they will have to be Mg, K, and P.

In PCT, a sample, in cylindrical shape, of more than twenty times the area compared to its volume is selected and immersed in distilled and deionized water. The leaching experiment is conducted for 7 days at a constant temperature of 90°C. At the end of the test, a sample of the leachate water is analyzed for the major elements of the waste form and the leaching rate is determined per unit area of the surface. Again, the results are included in Table 7 of this test on all four waste forms.

A third test is designed for hazardous metals defined by Resource Conservation and Recovery Act (RCRA) of the US Environmental Protection Agency [90].

The literature has been very scanty about the leaching index for contaminants from vitrified waste form and hence it is very difficult to make a comparison of the results presented in Table 7 with glass waste form. However, [85, 86] provide leaching index for various fission products on simulated tank waste streams in different waste forms. Generally their best results are >9 for the leaching index for any of the fission products. This may be compared with the results given in Table 7 for actual radioactive contaminants. In most cases, the results are several orders of magnitude higher than that for simulated waste forms reported earlier. (Note that increase in one number in the leaching index is a decrease by a factor of 10 in the diffusion constant, because  $LI = -\log(\text{diffusion constant})$ .) The only exception is that for iodine in M1 and Se in H1. In the first case the value is by one order less than 9, but in the other case it is still higher than 9 but not by several orders. Thus one may conclude that the CBPC technology performs far better than the expected performance of immobilized fission products waste forms.

Pacific Northwest Laboratory scientists conducted vitrification experiments for similar liquid waste streams [91] and measured the leach rate of the major constituents of the waste forms. Since boron, sodium, lithium, aluminum, and silicon are the constituents of their borosilicate glass, they conducted the PCT and measured the leaching rates for these elements. They show that the leaching results for the waste form of the stream AZ-102 (termed as H2 in Table 7) are 0.0063 g/m<sup>2</sup>·day for boron, 0.052 g/m<sup>2</sup>·day for sodium, 0.05 g/m<sup>2</sup>·day for lithium, 0.00786 g/m<sup>2</sup>·day for aluminum, and 0.033 g/m<sup>2</sup>·day for silicon, all higher than those observed for the major constituents of phosphate waste forms (see Table 7). This shows that it is not necessary to resort to high temperature-processes to immobilize secondary waste streams and room-temperature processes are capable of providing a rugged and leach resistant matrix for them.

Apart from the leach resistance of the waste forms, there are other issues. Radiolytic hydrogen [92] may be generated due to splitting of water and other hydrogen-containing molecules by intense radiation. Wagh et al. have conducted several studies on actinides in CBPC. When actual uranium and plutonium containing ash waste were immobilized, the radiolytic gas yield was 0.13 mol H<sub>2</sub>/100 ev, which is lower than that in cement waste form. Test details and comparative data may be found in [93]. This implies that the bound water in CBPC waste form did not play a major role in the gas yield.

In summary, CBPC technology is applicable to immobilization of the most acute high activity waste. It has been tested with actual waste and at full scale and is the best candidate for deployment in the current state of its art.

*4.3.2. Spent Nuclear Fuel [51].* In nuclear power plants, the nuclear fuel rods are used for the fission of nuclear material to produce electricity. They need to be changed every 10 years or so. These spent fuel rods are becoming a big liability for the nuclear industry and need long-term storage, because they are still highly radioactive when they come out of the reactor vessels. They irradiate neutrons and hence need to be stored for quite some time in water pools so that the irradiated neutrons are absorbed by water till they cool down and the neutron intensity depletes sufficiently so that they can then be stored in alternative dry storage casks and transported to permanent storage repositories.

The general composition of spent fuel is given in Figure 8 and the complete nuclear fuel cycle from power generation to waste form fabrication is presented in Figure 9.

As one may notice from Figure 9, once the uranium ore is milled and enriched, fuel rods are fabricated, which then are loaded into the reactor, where their high activity is used for power generation. After they become less efficient due to the decay process, they can be either used for reprocessing or may be simply sent for storage. Both options are used depending on the availability of sufficient fuel in every nuclear country. The spent fuel is stored in water pools with a hope of immobilization and ultimate storage in a repository as a glass waste form.

Unfortunately, in most countries, the fuel rods have remained in water pools because the logistics of building

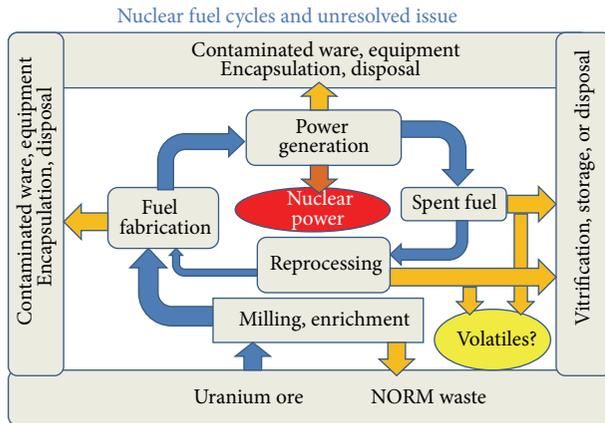


FIGURE 9: Nuclear fuel cycle and waste form production and the unresolved issue of volatiles.



FIGURE 10: Cross-section of a 55 gal drum scale surrogate salt waste form produced by P. R. Mayak in Russia with funding from USDOE and in collaboration with Argonne National Laboratory (2007) (source: Argonne file photo).

permanent repositories has not been resolved due to ecological issues and resistance from stakeholders and local authorities. Even if the repository issues are resolved, the spent fuel needs to be immobilized in a nonleachable and durable medium.

In the entire cycle, other high volume but low activity waste streams are generated too. These are either encapsulated in a cementitious waste form or simply stored in nonleachable drums in an underground repository such as Waste Isolation Pilot Plant (WIPP) in the United States [94].

The previous section on high activity liquid waste streams, the waste forms exhibit very high leaching resistance, comparable to that of glass waste forms. Since the vitrification technology is still not a full-fledged route to immobilization of spent fuel, the issue of volatile byproduct waste stream has not come to the forefront of the final scheme for handling the spent fuel. When the issue will come to the forefront, CBPC may turn out to be the most useful technology supplementing the glass waste form technology.



FIGURE 11: Demonstration samples of CBPC-based Borobond neutron shielding products. Source: Ceradyne Boron products website.



FIGURE 12: Demonstration of sewage pipe coating with Grancrete (Grancrete, Inc., Taipei, Taiwan) (<http://www.dynamo.com.tw>).

## 5. CBPC Products in the Market

The CBPC technology was initially developed for nuclear waste immobilization. Its first application was as a nuclear shielding material. Eagle Picher Technologies LLC perfected the technology by introducing boron in Ceramicrete, which was used and is probably still being used in US Department of Energy complex for waste immobilization and nuclear shielding. However its commercial product, named Borobond for shielding of neutrons was developed by Boron Department of Eagle Picher but now is owned by Ceradyne Corporation and hence 3M Company and is an established commercial product.

In structural materials area, the CBPC technology is well suited to fulfill needs for products that do not exhibit drawbacks of cement and polymer products. CBPC materials are inorganic and hence nonflammable. They exhibit negligible porosity and extremely low water permeability Table 2. They bond to all earth materials such as limestone, sand stone, and even conventional cement concrete. They also bond to

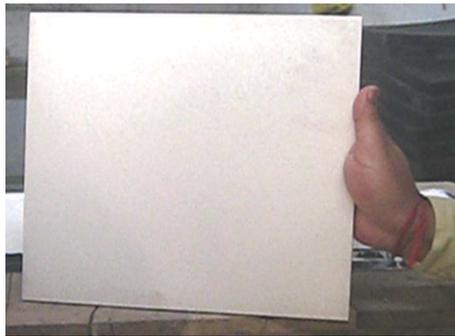


FIGURE 13: Insulated and solar reflective CBPC roof tile of in Chennai, India (<http://www.thermalcare.in>).

themselves. In the next section, we will see that, compared to other equivalent products, they are very environmentally friendly.

As was discussed briefly in Section 4.1, the structural products applications lie in two categories:

- (a) cements, grouts, and concrete,
- (b) coatings.

In both areas, several small businesses have made good strides in entering markets. For example, in the United States, Bindan Corporation of Oak Brook, Illinois (<http://www.bindancorp.com>) and Grancrete, Inc., (<http://www.grancrete.net>) of North Carolina have been in business for at least last 10 years producing road repair materials, concrete repair products, floor-surfacing products, and so forth. Grancrete has shown its presence in Taiwan and Japan for the same applications Figure 12.

Realizing that CBPCs are more expensive compared to Portland cement, CBPC concretes are not cost effective. Therefore, only value-added products are commercially viable. Because of this reason, recent trend has been to exploit unique properties of CBPCs and design products with performance superior to current products in the market.

One example is roof tiles named Thermal Care Tiles in Chennai, India (<http://www.thermalcare.in>). With CBPC formulations and additives, these tiles can reduce impact of hot sun in houses to the extent of 8–10°C by providing high reflectivity to solar radiation and also providing high thermal insulation properties Figure 13. CBPC-based coating products are probably the most unique ones among these. Eon Coat, Inc. (<http://www.EonCoat.com>), has introduced corrosion and fire protection coatings that exhibit outstanding properties. Their coatings do not show corrosion of the substrate or osmotic blistering [94] even when samples are exposed for 1000 hours in salt-spray chamber [95]. In the same way, the Flame Spread test [96] shows no flame spread at all and surpasses all organic coatings in performance. Learning the excellent performance of CBPC-based products, new companies are investing to develop range of products in the structural materials area.

There have been methodical attempts to develop bioactive dental and prosthetic cements using phosphates in the past [97] and also to exploit antibacterial properties of these

materials [98]. Since CBPC materials are phosphate based, they are uniquely positioned to match with composition of bones and teeth, in which hydroxyl apatite, a calcium phosphate hydrate, is the main component. Using modern CBPC for this application was conceived by Wagh et al. [99], and subsequent research led to root canal materials owned by Dentsply company. Following this, Bindan Corporation developed its own intellectual property [100] that led to a product called OsteoCrete marketed by Bone Solutions Inc. (<http://www.bonesolutions.net>) for multiple orthopedic solutions including bone void filler. Tay et al. [101] have provided the most recent advances in this area.

There have been many other areas in which preliminary work has been done in application of CBPCs, but commercial exploitation has not occurred as yet. Notable areas are CBPCs for oil fields [102–104] and fiber reinforced products [68, 105].

In summary, CBPC technology and its products, and Ceramicrete in particular, have entered various markets in different parts of the world. The new products have potential to be transferred from small businesses to larger ones. Borobond, the first product, has been a good example of this, which was developed by Eagle Picher and then went to Ceradyne, a bigger company, and now 3M Company owns Ceradyne. Such acquisitions may provide much wider visibility to unique CBPC products.

## 6. Environmental Effects of CBPC

CBPCs are mineral based materials like Portland cement. Therefore, the main environmental effect parameters seen in use of these materials are similar to that of Portland cement. These include, greenhouse gas emissions and fugitive particulates released in the atmosphere. While the latter can be controlled with good work practices, the first one is built in the chemistry of the process itself and cannot be avoided.

There are two major sources of greenhouse gases in these technologies. Carbon dioxide is bound in the raw materials such as limestone and dolomite, which escapes during extraction of the appropriate raw material. This may be termed as the direct emission.

The second source of greenhouse gas emission is the energy consumption in producing the final product. This includes carbon dioxide generated by the energy use in mining of appropriate minerals, their transport, extraction of the desired ingredients for the product, production operations, packaging, and shipping. Emissions resulting from these may be called process emissions. Process emissions may be reduced only by reducing energy consumption and thereby release of greenhouse gases.

The direct emissions in Portland cement manufacture and CBPCs are different because the two products use different raw materials. However, operations from manufacture to shipping are very similar in both cases and hence one can assume that their process emissions are also similar though not the same.

US Environmental Protection Agency (EPA) has provided guidelines for calculation of direct emissions [106]. Following that we have calculated direct emissions from the CBPC manufacture and compared that to the emissions in

TABLE 2: Water permeability and mechanical properties of CBPC with wollastonite and other fillers [29].

Binder	Composition (wt.%)		Strengths (psi)		Fracture toughness (MPa·m <sup>1/2</sup> )	Water absorption (wt.%)
	Wollastonite	Other	Compressive	Flexural		
40	60	Nil	8,426	1,474	0.66	2
50	50	Nil	7,755	1,236	0.63	2
30	30	Sand 40	6,264	1,255	0.63	3
100	Nil	Nil	3,500	1,100	N/A	15
40	Nil	Ash 60	11,507	1,474	0.19	1.78
Typical Portland cement concrete			8,000	940	N/A	10–20

TABLE 3: Specific activity and boiling point of fission products [62, 63].

Fission product	Half-life (yrs)	Specific activity (Ci/g)	Boiling point (°C)
Sr-90	28	140	1384
Cs-137	30	870	678.4
Cs-135	3E + 6	0.0012	678.4
Tc-99 (as NaTcO <sub>4</sub> )	2.1E + 5	0.17	100
I-131	18.02 days	>5,000	184

cement sector. Taking the example of Ceramicrete as a CBPC, the actual calculations are provided in the appendix. These calculations show that direct emissions from Ceramicrete manufacture are 40% less than that in manufacturing of cement. This is mainly because Ceramicrete contains 60% fly ash, which is an industrial byproduct from the utility industry and direct emission contribution to this component is zero.

Assuming the process emissions are the same for the same tonnage of both products, when the direct and process emissions are added, Ceramicrete emits only 20% less greenhouse gases compared to Portland cement. Thus there is no substantial gain in using CBPCs cement.

As we have seen in Section 5, CBPCs are also used as inorganic coatings. Here they can be environmentally very friendly alternatives to polymer coatings. This is because CBPC coatings are the first inorganic alternatives to organic coatings. Therefore, CBPCs can make a big difference in the coating world. This may be seen in the following analysis.

The ecological impact of CBPCs arises from four major factors, which are described in [67]:

- (a) greenhouse gas emissions,
- (b) low-level ozone emissions,
- (c) acidification,
- (d) eutrophication.

Greenhouse gas emissions are the same as the direct emissions discussed above in context of cement industry. Low-level ozone emissions result from release of volatile organic compounds (VOCs) into the environment during manufacturing of organic paints and their use. Acidification, on the other hand, is due to sulfur in the polymers that results in formation of oxides of sulfur and eventually sulfuric acid, which is harmful to the nature.

We can use the numbers from the appendix for greenhouse gas emissions. Ozone depletion is nonexistent in the case of CBPCs because there are no VOCs in CBPC coatings. Acidification is also not an issue because CBPC coatings do not contain sulfur compounds. They contain phosphate compounds, but phosphate release is negligible as has been shown in several Product Consistency tests (see, e.g., PCT data in Table 4). Thus acidification is not an issue.

The fourth factor, eutrophication [107], is the result of leaching of nutrients into soil and water streams that produce unwanted algal growth, which chokes aquatic life and plant growth. CBPCs contain significant amount of phosphates. They are also good fertilizers and their presence in aquatic streams can be a problem. Fortunately, Product Consistency leaching results presented in Table 7 conducted by us have shown that CBPC products release phosphates extremely slowly into ground water and hence good CBPC products should not affect the environment. These conclusions are very preliminary and detailed investigations are needed in this area for a given application.

In light of these observations, we have summarized the benefits of CBPC coatings over polymeric coatings in Table 8. For the sake of calculations, we have assumed the coating composition is the basic Ceramicrete binder (MgO and monopotassium phosphate and 35% water in the coating).

Table 8 shows that CBPC coatings produce only about 15% of solvent-based varnish and 80% of solvent-based alkyd paint. They produce no ozone damaging VOCs nor any oxides of sulfur that lead to acidification. Their potential for eutrophication is negligible because CBPC coatings are like phosphate minerals and leaching of phosphate in the environment is minimal.

## 7. Conclusions

CBPCs, in a period of 20 years, have made major strides in various fields from nuclear waste immobilization, safe storage of nuclear materials, and structural products and in dental and prosthetic applications. The first ten years were invested in understanding the chemistry of these materials as well as length and breadth of their possible applications and carving out focus areas for products development. The last ten years have seen them entering the market all over the world.

CBPCs were invented primarily to immobilize low-level radioactive waste. In last 10 years, however, research has demonstrated that they may as well be used to tackle the

TABLE 4: Waste streams tested in the Russian project [64].

Nature of the contaminant	H1	H2	M1	M2
Waste source	Supernatant from Hanford, AN-105	Supernatant from Mayak, Russia	Sludge from Hanford, AZ-102	$\alpha$ -Bearing waste from Mayak, Russia
Solids content (wt.%)	52	38	35	16
Major benign ions (g/L)	Na <sup>+</sup> -256 NO <sub>3</sub> <sup>-</sup> -167 NO <sub>2</sub> <sup>-</sup> -113 OH <sup>-</sup> -84	Na <sup>+</sup> -265 NO <sub>2</sub> <sup>-</sup> -85 OH <sup>-</sup> -43	Na <sup>+</sup> -99 NO <sub>3</sub> <sup>-</sup> -38 NO <sub>2</sub> <sup>-</sup> -295 OH <sup>-</sup> -90	Na <sup>+</sup> -83 NO <sub>2</sub> <sup>-</sup> -24
Activity of actinides (Bq/L)	<sup>239</sup> Pu-1.2E8 <sup>237</sup> Np-1.2E8	<sup>239</sup> Pu-3.5E8 <sup>237</sup> Np-2.4E6 <sup>241</sup> Am-8.0E8		Sa-1.3E5
Fission products	<sup>90</sup> Sr-2.1E7 <sup>137</sup> Cs-2.4E7 <sup>99</sup> Tc-6.3E8 <sup>131</sup> I-1, 1E7 <sup>75</sup> Se-2.7E6	<sup>90</sup> Sr-5.1E8 <sup>137</sup> Cs-1.2E7 <sup>99</sup> Tc-1.9E9	<sup>90</sup> Sr-1.5E6 <sup>137</sup> Cs-5.8E10 <sup>99</sup> Tc-6.3E8 <sup>129</sup> I-2.3E6	
Hazardous metals	Cr-2.9 as CrO <sup>4+</sup> Pb <sup>2+</sup> -0.07 Cd <sup>2+</sup> -0.003	Cr <sup>3+</sup> -0.24 Pb <sup>2+</sup> -0.01 Cd <sup>2+</sup> -5 Ni <sup>2+</sup> -2.4	Cr-7 as CrO <sup>4+</sup>	Ni <sup>2+</sup> -2.4

TABLE 5: Neutralization and stabilization additives.

Issue	Additive
Neutralization of alkaline streams	Small amount of H <sub>3</sub> PO <sub>4</sub>
Tc <sup>+7</sup> (in pertechnetate state)	<0.5% SnCl <sub>2</sub> [64]
I <sup>-</sup>	AV-17 resin in Cl <sup>-</sup> form
Cs and Sr	K <sub>4</sub> [Fe(CN) <sub>6</sub> ] · 3H <sub>2</sub> O

TABLE 6: Physical properties of the waste forms.

Loading and properties	H1	H2	M1	M2
Waste loading	35	44	43	34
Density (g/cm <sup>3</sup> )	1.6-1.7	1.7-1.8	1.8	1.8
Compressive strength (MPa)	25-55	40-55	>20	>20

most difficult issue of volatile high activity fission products, where high temperature technologies fail. They have entered the market as nuclear shielding materials in an aggressive way.

Because CBPCs can be used as grouts or coatings, applications may extend well beyond what we see in the market. They have zero flame spread and high reflectivity to infrared radiation and may be used very widely in fire protection and insulation. They have shown excellent corrosion protection of steel. Therefore, they may turn out to be the first inorganic corrosion protection coatings. Efforts are underway in the industry to bring CBPC products in the market in these fields.

All this has happened with only one composition of magnesium oxide and monopotassium phosphate, known as Ceramicrete. Potential to develop products lies well beyond the current state of the art, because a wide range of other formulations is feasible. It is hoped that the fundamental work reported during the first 10 years and applications-oriented progress during the last 10 years will lead to wider curiosity

TABLE 7: Results of leaching results.

Contaminants	H-1	H-2	M-1	M-2
ANS 16.1 90-day immersion test for radioactive contaminants [65]				
Actinides				
<sup>237</sup> Np	12.8	13.6		
<sup>239</sup> Pu	13.5	14.4		Total alpha = 12.9
<sup>241</sup> Am		14.6		
Fission products				
<sup>90</sup> Sr	10.9	13.2	11.1	
<sup>137</sup> Cs	11.4	11.5	13.0	
<sup>99</sup> Tc	9.9	10		
<sup>231</sup> I	11.2		7.9	
<sup>75</sup> Se	9.6			
PCT 7-day immersion test at 90°C for product constituents (g/m <sup>2</sup> ·day as normalized leaching rate [66])				
Mg	4.1E-6	7.1E-7	6.6E-5	1.6E-5
K	1.9E-2	1.1E-2	2.4E-2	2.4E-2
PO <sub>4</sub>	6.3E-3	1.8E-3	7.2E-3	9.5E-3
Na	1.7E-2	9.3E-3	2.4E-2	2.1E-2
Toxicity characteristic leaching procedure for hazardous elements (ppm) [66]				
Element	Reg. limit			
Pb	0.75	0.005	0.004	0.08
Cr	0.6	0.04	0.006	0.2
Cd	0.11	0.001	0.008	
Ni	11.0		<0.1	0.5

in these materials and result in more investment and products development.

TABLE 8: Comparison of environmental impact factors of CBPC and typical commercial coatings. Data for commercial coatings is reproduced from [67].

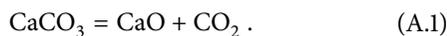
Coatings	Direct emissions (g/kg)	Low-level ozone (g ethane/kg)	Acidification (g Sox/kg)	Eutrophication (g P <sub>2</sub> O <sub>5</sub> /kg)
Solvent-based varnish				
Binding agent	881.6	4.2	7.4	0.9
Solvent	1145.7	2.1	6.8	0.7
<b>Total</b>	<b>2027.3</b>	<b>6.3</b>	<b>14.2</b>	<b>1.6</b>
Solvent-based alkyd paint				
Binding agent	283.4	0.8	3.2	0.3
Filler	25.3	0.01	0.3	8.3
Solvent	63.9	0.3	1.0	0.1
<b>Total</b>	<b>372.6</b>	<b>1.11</b>	<b>4.5</b>	<b>8.7</b>
CBPC coatings	300	0.0	0.0	Very low but to be quantified

## Appendix

### Calculations of Direct Emissions from CBPC Production

One ton of Portland cement produces one ton of CO<sub>2</sub>. It consists of two parts, direct emissions resulting from decomposition of limestone into CaO and CO<sub>2</sub> and the rest from process parameters such as fuel consumption, transport of raw materials, grinding and sieving operations, and transport and shipping. Direct emissions can be calculated from chemistry and thermodynamics, while the process emissions are site specific and must be monitored and determined at each plant [67]. This is also true for CBPC cement products also. However, due to process similarities, it is quite likely that the process emissions in both cases will be similar. For this reason, we will calculate the direct emissions and compare the environmental benefits of CBPCs.

1. *Calculation of Direct Emissions in Portland Cement Production.* Direct emissions in Portland cement manufacture arise from clinkering limestone (calcium carbonate) at 1500°C to produce calcium oxide by the decomposition



Molar weights of CaO and CO<sub>2</sub> are 56 and 44 g/mole.

Portland cement contains approximately 64 wt.% CaO, with the rest being silica and alumina. Therefore, direct emission of CO<sub>2</sub> to produce one ton of cement is

$$\text{molar weight of CO}_2 / \text{molar weight of CaCO}_3 \times 0.64 = (44/56) \times 0.64 = 0.5.$$

This means direct emission is 05 kg/kg of cement and 0.5 kg/kg of CO<sub>2</sub> because of other production and distribution processes.

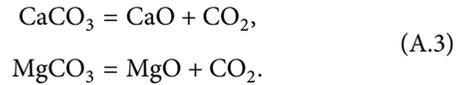
2. *Calculation of Direct Emission in Ceramicrete Production.* Composition of Ceramicrete is 10 wt.% MgO + 30 wt.% MKP + 60 wt.% fly ash. MgO is produced from dolomite rock, which is MgCa(CO<sub>3</sub>)<sub>2</sub> or MgCO<sub>3</sub> + CaCO<sub>3</sub>. It is again calcined at 1500°C and MgO and CaO are separated.

Assuming equimolar proportion of MgCO<sub>3</sub> and CaCO<sub>3</sub> in dolomite rock, the proportion of MgCO<sub>3</sub> and CaCO<sub>3</sub> is 45.7 wt.% to 54.3 wt.%. This gives us

$$\begin{aligned} \% \text{MgO content} &= \text{MgO} / \text{MgCO}_3 \times 45.7 \\ &= 0.403 \times 45.7 = 18.28\%. \end{aligned} \quad (\text{A.2})$$

This means kg of dolomite rock will produce 182.8 g of MgO.

Total amount of CO<sub>2</sub> released during calcination of dolomite comes from decomposition of CaCO<sub>3</sub> and MgCO<sub>3</sub>. The decomposition equations for the two components are



Using molar weights of the components, we find that CO<sub>2</sub> content in dolomite rock is 47.8 wt.%. Thus,

$$\text{CO}_2 \text{ produced per ton of MgO} = \frac{47.8}{18.28} = 2.59 \text{ tons.} \quad (\text{A.4})$$

Ceramicrete contains 10 wt.% MgO. Therefore, Ceramicrete produces 25.9 g of CO<sub>2</sub> per kg of Ceramicrete because of use of MgO in it.

Similarly, monopotassium phosphate also produces CO<sub>2</sub>.

MKP is produced from potassium carbonate by reacting it with phosphoric acid, during which CO<sub>2</sub> is released as given in the equation below:



Molar weights of K<sub>2</sub>CO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, and KH<sub>2</sub>PO<sub>4</sub> are 124, 98, and 272 g/mole, respectively. So to produce 272 kg of MKP, we produce 44 kg of CO<sub>2</sub>.

This means to produce one kg of MKP, we produce 44/272 = 0.16 kg of CO<sub>2</sub>.

Thus, contribution of CO<sub>2</sub> due to MKP = 0.3 × 0.16 = 0.048 kg/kg of Ceramicrete. Therefore, total direct emission, which is the sum of emissions due to MgO and MKP production, is

$$0.259 + 0.048 = 0.3 \text{ kg/kg of Ceramicrete.} \quad (\text{A.6})$$

This is 60% of direct emission in cement production.

3. *Total Emission Reduction.* Since both processes use very similar processing technology, we assume the process emissions to be similar, equal to 0.5 ton of CO<sub>2</sub>/kg:

$$\text{total emission in Ceramicrete} = 0.3 + 0.5 = 0.8 \text{ ton of CO}_2 / \text{kg of Ceramicrete,}$$

total emission in cement =  $0.5 + 0.5 = 1$  kg/kg of cement.

The paper is intended to disseminate scientific progress in the subject explained to a wider scientific audience with the hope that it will lead to further research and development in this field for the benefit of a wider international community.

## Conflict of Interests

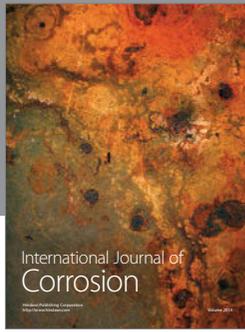
The author declares that he has no financial interest in writing this paper.

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