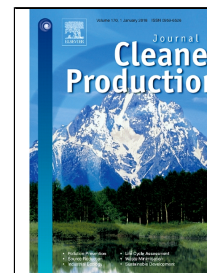


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Highlights:

- Phosphate bonding and alkali-activation of tailing minerals
- Ceramic-like materials vs. hydraulic cements
- Research gaps identified: potential of pre-processing
- Relatively new research field with potential

Recycling mine tailings in chemically bonded ceramics – A review

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Mine tailings account for most of the environmental incidents related to the extractive industry, with risks increasing due to steadily rising tonnage of low-grade ore and extreme weather events. Recycling of tailings in raw-material-intensive applications presents an interesting alternative to costly tailings management with associated restoration efforts. Chemically bonded ceramics may offer a route to upgrading mine tailings into raw materials for ceramics. In this review such chemically bonded ceramic methods that may be used to recycle mine tailings as raw materials, are reviewed while focusing in particular on two methods: 1) geopolymerization/alkali activation and 2) chemically bonded phosphate ceramics. The aim of the review is not to give exhaustive review on the wide topic, but to scope the required boundary conditions that need to be met for such utilization. According to the findings, alkali activation has been studied for 28 separate silicate minerals in the scientific literature, and presents a viable method, which is already in commercial use in calcium-rich cement-like binder applications. Phosphate bonding literature is more focused on phosphate containing minerals and waste encapsulation. Very little work has been done on low-calcium tailings utilization with either technology, and more knowledge is needed on the effect of different pre-treatment methods to increase reactivity of mine tailings in chemically bonded ceramics.

1. Introduction

In the effort towards circular economy and waste minimization, mining waste is one of the foremost industrial side streams needing the attention of the scientific community due to the large volumes in question. Mining wastes are produced by the extractive industry and is currently one of the largest waste streams in the world. Mine tailings are stored either in dammed ponds along with the process water or as thickened pastes in piles usually near the mine sites. Lottermoser (2010) estimates that approximately 20-25 billion tons of solid mine wastes are produced annually in the world, of which 5 to 7 billion tons are mine tailings (Mudd and Boger 2013). According to other estimates it is up to 14 billion tonnes (Jones and Boger 2012), and is bound to increase due to higher utilization of low grade ores in the future.

The implementation of Directive 2006/21/EC on the management of wastes (European Parliament and the Council of the European Union 2006) is adding pressure to the extractive industry to adapt new disposal practices with low environmental risks and to increase utilization of mine tailings. Tailings can be a significant resource, as more and more research has been recently focused on their applicability for geopolymers (Ahmari and Zhang 2012, 2013; J. Castro-Gomes et al. n.d.; P. Duxson et al. 2007; Jenni Kiventerä 2016; Provis, Palomo, and Shi 2015; L. Zhang 2013) and for new minerals resources and sources for critical metals, e.g. Co, REE (Weber, Leek, and Alzubairi 2015; EU project ProMine 2008). Indeed, in order to reach better environmental, social and economic outcomes of tailings management across an integrated approach has been called for including orebody characterization, mine planning, processing, disposal, reprocessing, recycling and reuse (Edraki et al. 2014). Recycling and reuse are *Reuse* of mine tailings can be defined as the process involving the new use of the total waste in its original form for a specific purpose directly without any reprocessing (B. G. Lottermoser 2011). In contrast, by applying some reprocessing the waste can be *recycled* as feedstock to convert the entire mine waste into a new valuable product or application. Reusing is regularly done in close vicinity to the mining site, and covers low-value applications such as sand-rich tailings mixed with cement and used as backfill in underground mines, and clay-rich tailings as an amendment to sandy soils for the manufacturing of bricks and floor tiles. Tailings of certain mineral composition may have particular reuse and recycling potential, such as phlogopite-rich tailings to trap phosphorus from waste waters (Hartikainen and Helinä Hartikainen 2008), and ultramafic tailings as feedstock for rock wool insulation (Marabini et al. 1998).

The use of non-toxic mine tailings as a raw material for ceramics has no fundamental hindrance other than the potential complexity of the mineralogy. Producing functional polycrystalline ceramics conventionally from powdery raw materials requires high temperature processing (hot isostatic pressing, sintering etc.),

since diffusion through solid matter is required in order for a dense structure with adequate mechanical strength to form (Lange 1989). High level of purity and homogeneity of powders are requirements for successful sintering, which translates into long and expensive processing chains for raw materials. A ceramic application with a forgivingly wide mineralogical range is glass-ceramics, where the main glass network formers are SiO_2 and Al_2O_3 , both prevalent in mine tailings. Indeed, glass ceramic have been made utilizing tailings from gold (Shao et al. 2005), rare Earth (Baowei et al. 2013), chromite and talc mines as well all red mud from aluminum extraction (Marabini et al. 1998). Another approach, which in addition does not require sintering, is chemical bonding utilized in the processing of *chemically bonded ceramics (CBC)*.

Ceramics are unmatched in their capability to withstand oxidative and corrosive environments in industrial processes, where extremes of temperatures and pH are common. Their ability to cope in these harsh environments stems from the inherent properties of the dominating chemical bonds. In the covalent and ionic bonds that dominate in ceramic materials, electrons are in low-energy configurations, turning the material less prone to interact with its environment. This inherent inertness of ceramic material is what makes them superior in many applications, and therefore it is useful to draw a distinction between materials by the dominating chemical bonds (Figure 1).

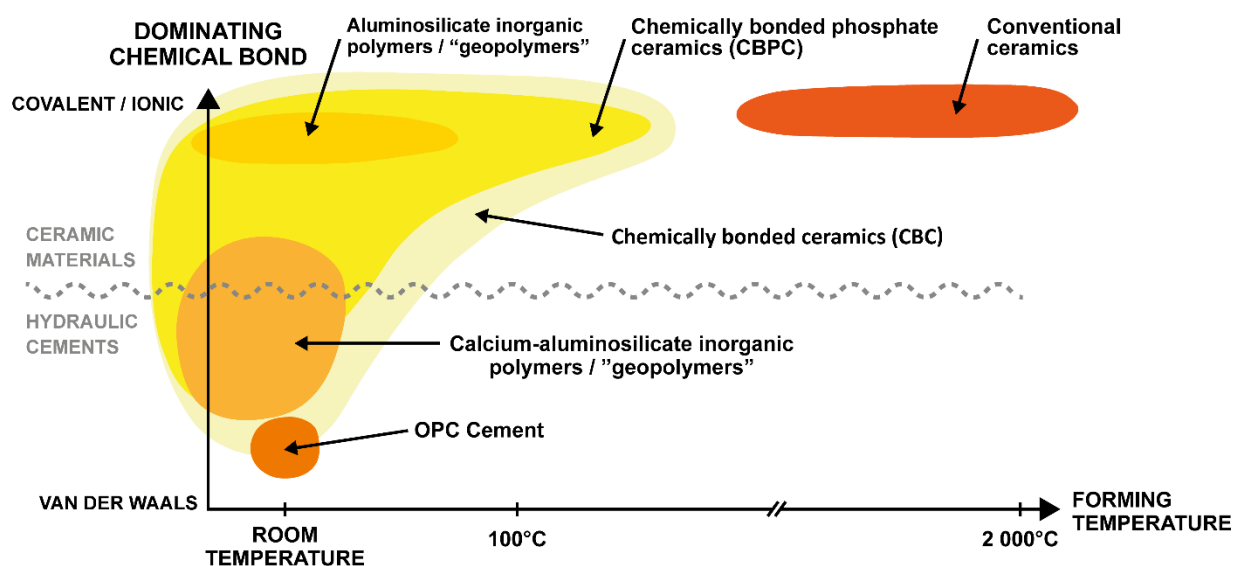


Figure 1: The framework used to distinguish materials by the dominating chemical bonds. Common inorganic materials can be separated by their dominating chemical bonds and formation temperature, highlighting the difference between hydrated materials and covalent-dominated materials. Ceramic-like materials are the focus of this paper (dominated by covalent/ionic bonding).

Chemically bonded ceramics describes a group of inorganic materials that share properties with both cements and ceramics. The formation of CBCs happens by chemical route, much like with conventional cements, while the chemical bonds and mechanical properties resemble those of ceramics (see Figure 1). Chemically bonded ceramics offer a potential alternative ceramic processing route, where high temperatures are not required and solid structures formed in ambient temperature in the presence of mineral impurities. Robustness with regards of mixed mineralogy is partly due to insolubility of unwanted minerals; soluble phases take part in the binder formation, while insoluble minerals function as fillers in the final composite structure.

The **motivation** for this review was therefore to study if chemically bonded ceramics could be made from impure raw materials (mine tailings) using non-standard processing methods (CBC's). The **focus** is on two methods: alkali-activation, and phosphate bonding. The **research question** was to find out if these two methods have potential in using mine tailings as raw material for ceramics. This review is a non-exhaustive review of literature, but aims to give a broad picture of the area of research, and to identify gaps in knowledge. There has been multiple reviews about mineral waste recycling in alkali-activated materials (Komnitsas and Zaharaki 2007; Rao and Liu 2015; Bernal et al. 2016; Sedira et al. 2017) and in construction materials in general (L. Zhang 2013; Velasco et al. 2014), but this is the first review focusing on *ceramic-like* end products from mine tailings, a distinction that is illustrated in Figure 1. Furthermore, an attempt is made to analyze the suitability of raw materials by their *mineralogy*, rather than the source of origin. This is a key distinction given that it is the mineralogy, not source or even chemical composition, that governs the reactivity, which is the main bottleneck in the processing of chemically bonded ceramics.

In the following chapters, the literature is reviewed on two potential processing methods for CBCs and their suitability for mixed-mineralogy raw materials, such as mine tailings. The suitability is assessed by evaluating the following aspects in the reviewed literature:

- 1) Applicability of common minerals in mine tailings
- 2) Robustness towards unwanted components
- 3) Track record in industrial applications

The structure of the paper is the following: the review is split into three main sections where first the mine tailings are introduced, and the two following chapters are devoted to the chemically bonded ceramic processing methods: 1) geopolymers/alkali-activated materials and 2) chemically-bonded phosphate ceramics (CBPC). At the end, the future of the tailings utilizations and the need for future research are discussed.

2. Methods and scope

As this is the first review in a new field, structured review on the topic was not possible due to non-comparable research methods. Instead, a loosely structured process was used that consisted of keyword search, identification of relevant work, summarizing and interpretation in an iterative loop. A non-exhaustive review was conducted using conventional content analysis methods, where information is derived directly from the text data with the aim of scoping the potential of the chemically bonded ceramics methods in utilizing mine tailings as raw material, and identifying gaps in the knowledge related to that.

The review is based on literature from the entire world, and includes studies reported in peer-reviewed journals, books and patents written in English. Papers were searched by combination keyword searches on major databases and publisher websites (Google Scholar, Scopus, Ebsco, Springerlink, Wiley Interscience, Elsevier ScienceDirect). Keywords such as "alkali-activation", "alkali-activated materials", "AAM", "geopolymer", "phosphate ceramics", "chemically bonded ceramics", "CBC", "CBPC", "phosphate", were combined with "mine tailings", "mining residue", "waste", and "extractive industry", "valorization of tailings", and "tailings impoundment".. An area of considerable potential and research interest is also the use of (processed) mine tailings in alkali activated *cements* and *cementitious* composites (L. Zhang 2013; Fernando Pacheco-Torgal et al. 2014). These construction materials promise perhaps the lowest-hanging fruits in terms of commercial utilization of mine tailing due to environmental benefits and low cost of manufacture (McLellan et al. 2011; G. Habert, d'Espinose de Lacaillerie, and Roussel 2011). However, they are mostly left outside of this review due to the high amount of calcium (>10%) which results in calcium hydrate end-products, held together partly by Van der Waals forces. As a result they are more akin to conventional hydraulic cements than ceramics (see Figure 1), and the interested reader is directed to an excellent recent review (Bernal et al. 2016).

3. Introduction to mine tailings

The environmental impacts of tailings are several. Acid mine drainage is the most common and worldwide environmental hazard caused by the extractive industry. Exposure of sulfide minerals to air and water is the main acid-producing process. Dam falls and seepage waters from waste facilities affect groundwater and surface water. Acidity and high iron, aluminum, metal, and sulfate contents are characteristic for acid mine drainage (Nordstrom DK 1999). Metals and other toxic compounds releasing in the environment spoil waterways and accumulate in plants and animals and eventually to humans.

Failure of the tailings storage may have large-scale effect on the financial performance of the mine (Dawson, Phillip, and O’Kane 2009). The costs of cleaning combined with the loss of so-called ‘social license to operate’ (approval of the locals) and bad reputation may lead, at worst, to environmental disaster and closure of the mine. In industrialized countries, several laws are controlling waste management and treatment. Strict legislation and using best available techniques (BAT) protect the environment from contamination and major catastrophes caused by dam falls. Even though strict compliance of the laws and requirements is expensive, the investment is cost effective (Kossoff et al. 2014).

Tailings’ characteristics markedly depend on mineralogy of the ore deposit and the refining method selected. One feature typical for tailings pond is grain size differentiation. Sand and silt rich layers alternate throughout tailings bed (Parviainen et al. 2012; Heikkinen and Räsänen 2008). For example fine tailings from Cu-W mine have 60-90% of <0.063 mm and fine to medium sand tailings 70% of 0.063-0.595 mm. Quartz predominates tailings from massive volcanic sulphide ores (Heikkinen and Räsänen 2009). Feldspars are typical for tailings from felsic (silicon rich) ore types (Figure 3), and their quantity is decreasing in tailings from mafic to ultramafic ore types (Heikkinen and Räsänen 2008, 2009; Parviainen 2009). Table 1 shows chemical compositions of two tailings types from mafic ores and that of tailings from Outokumpu type massive sulphide ore.

Table 1: Oxide compositions of tailings from a Ni-Cu sulphide ore (Hitura), talc production, and Cu-Co-Zn-Ni sulphide ore (Polvijärvi, Luikonlahti respectively). (Heikkinen and Räsänen 2009)

Ore deposit	SiO ₂ (%)	MgO	Fe ₂ O ₃	Al ₂ O ₃	CaO	K ₂ O	Na ₂ O	S
Ni-Cu	38,8	32	13,9	2,94	0,89	0,41	non	1,25
Talc	19,1	36,9	9,09	0,91	2,64	0,02	non	0,96
Cu-Co-Zn-Ni	56,9	7,39	17,3	3,41	6,37	0,7	0,67	7,63

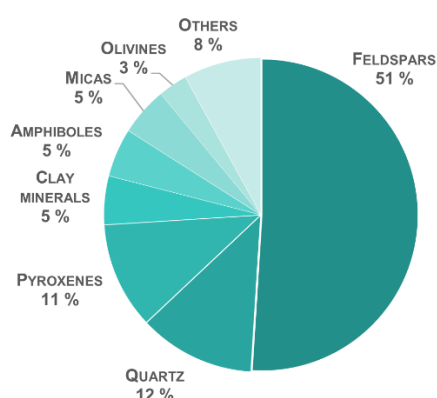


Figure 2: Abundance of main minerals in earth’s crust, which reflects the typical mineralogy of tailings from felsic ore deposits. Data by Ronov and Yaroshevsky (1969).

A mineral processing method of metalliferous hard rock deposits and industrial mineral deposits involves crushing and powdering (milling) the ore, flotation and in some cases also leaching of valuable minerals from gangue minerals. Ore refining methods depend on the properties of the ore and the host rock.

Chemical additives are employed for the refining and/or leaching the ore minerals from the gangue phases. Concentrates containing the ore minerals are recovered, and residuals rich in gangue minerals are disposed as tailings in dammed impoundments. Tailings are classified hazardous wastes if they contain harmful substances such as metals, radioactivity, acid- generating minerals, and process chemicals. However, many tailings are ordinary, less hazardous wastes with low or no harmful components.

The minerals in tailings become non-evenly distributed spatially, which makes their utilization more difficult. In general, tailings combined with the process water are pumped in the form of slurry through a pipeline from the mill (concentrator) to the impoundment. In the impoundment, the streaming slurry deposits solid particles in a manner similar to sedimentation in water basins. This sedimentation creates grain size and mineralogical differentiation inside the tailings impoundment: coarser and heavier particles settle near the discharge pipe, while the smallest and finer material flows longer distance (Blight, G.E. and Bentel, G.M. 1983) and settle in depressions. Especially in depressions, particle size is vertically distributed. The grain size and mineralogical differentiation gets more complicated if there are several discharge pipes and when the pipes positions are changed. Additionally, the tailings content and quality in impoundments can vary according to changes in ore deposit types.

4. Geopolymers and alkali-activated materials (AAM)

Alkali activation is a platform technology for utilization of inorganic wastes and industrial residues and providing a path towards more sustainable inorganic construction materials. This chemical bonding process exhibits robustness and flexibility simultaneously — the properties of the end-product can be tuned by the chemical composition of the precursors, but at the same time, the process is relatively insensitive to non-crucial chemical components. This insensitivity provides the capability of utilizing industrial side streams as raw materials. There are many recent reviews on alkali activation (Provis, Palomo, and Shi 2015; Bernal et al. 2016), and this review is focused on literature that is specific to mine tailings and minerals encountered there.

Typically, alkali activation proceeds by mixing aluminosilicate precursor, a powdery solid, with activator that is liquid. Suitable geopolymer precursors must be rich in reactive aluminate and silicate groups that dissolve and form an aluminosilicate network during the alkali activation process. Activator that initiates the reaction, commonly sodium or potassium hydroxide, also serves a second purpose: the aluminosilicate network consisting of tetrahedrally coordinated SiO_4 and AlO_4^- groups is negatively charged and needs to be charge balanced by the Na^+ or K^+ ions of the activator.

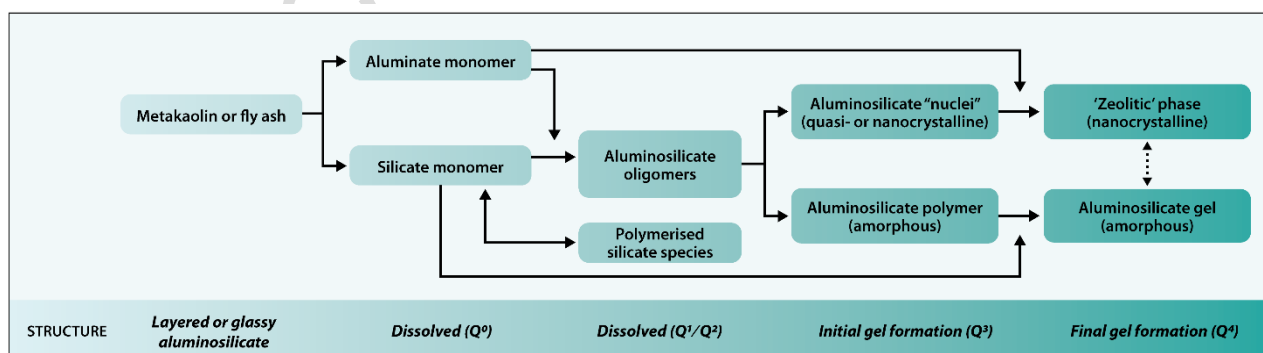


Figure 3: Conceptual model for alkali-activation of low-calcium solid precursor such as metakaolin, adapted from (Provis 2014).

The amount of calcium in the precursors has a major effect on the microstructure and indeed on the nature of chemical bonds present in the solidified material. Specifics of the microstructure are under debate, but it is agreed upon that the case of high calcium (>10%) results in hydration products of calcium, sodium, aluminum and silicon where water is part of the final structure, which is similar to OPC cement, albeit with more cross linking between the layers (Myers et al. 2013). Low-calcium system—schematic shown in Figure 3—results in a highly cross-linked gel, that is dominated by short range covalent bonding and where water plays no major role after the initial formation of the bonds (Provis, Lukey, and van Deventer 2005).

4.1. Applicability of alkali activation to commonly available minerals in mine tailings

Mine tailings present a potential precursor source for geopolymers: the most abundant minerals in the Earth's crust are aluminosilicates (i.e. alkali feldspars), which is also reflected in the tailings compositions. However, the alkali-reactivity of the mine tailings is generally low, and it presents the most critical aspect in tailings-based alkali activation. Therefore, pretreatments are necessary in order to increase the reactivity.

The property of a potential precursor that chiefly dictates its reactivity in geopolymer processing is the alkali-solubility of aluminum, which in turn is dictated by its mineralogy. Previous research done on finding suitable precursors includes a wide selection of studied aluminosilicate minerals. Table 2 presents a non-exhaustive list of the reactivity of different aluminosilicate minerals as geopolymerization precursors. One of the first, and still the most comprehensive screening of minerals in geopolymerization has been done by Xu and Van Deventer (2000). The tested minerals were mixed with metakaolin in order to increase reactivity, and therefore the results cannot be directly compared with other findings in the literature.

Table 2: The potential of minerals as geopolymer precursors from scientific literature

MINERAL	IDEAL STOICHIOMETRY	CLASSIFICATION	REACTIVITY IN GEOPOLYMERIZATION	LITERATURE
ALBITE	$\text{NaAlSi}_3\text{O}_8$	Tectosilicate/ Feldspar family	Combined with kaolin Good (1-part mix). Heated to 1000 °C with 50% NaOH	(Xu and Van Deventer 2000, 2003) (Feng, Provis, and van Deventer 2012)
ALKALI-FELDSPAR (K)	KAlSi_3O_8	Tectosilicate/ Feldspar family	Acceptable (activated with 5 M NaOH + Na_2SiO_3)	(Xu and van Deventer 2003; Ahmari and Zhang 2012)
ALKALI-FELDSPAR (NA)	$\text{NaAlSi}_3\text{O}_8$	Tectosilicate/ Feldspar family	Acceptable (better when activated with 5 M KOH + Na_2SiO_3)	(Xu and van Deventer 2003)
ALMANDINE	$\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$	Neosilicate/Garnet group		(Xu and Van Deventer 2000)
ANDALUSITE	Al_2SiO_5	Neosilicate/ Al_2SiO_5 group		(Xu and Van Deventer 2000)
ANORTHITE	$\text{CaAl}_2\text{Si}_2\text{O}_8$	Tectosilicate/Feldspar family		(Xu and Van Deventer 2000)
AUGITE	$(\text{Ca}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_2\text{O}_6$	Chain silicate/ Diopside—hedenbergite series		(Xu and Van Deventer 2000)
CELSIAN	$\text{BaAl}_2\text{Si}_2\text{O}_8$	Framework silicate		(Xu and Van Deventer 2000)
CLINOPTILOLITE	$(\text{Na}, \text{K}, \text{Ca})_2\text{Al}_3(\text{Al}, \text{Si})_2\text{Si}_{13}\text{O}_{36} \cdot 12\text{H}_2\text{O}$	Tectosilicate/zeolite	Mixed with albite, calcite and montmorillonite	(Bondar et al. 2011)
GRANITE	< 20% quartz and > 65% alkali feldspar	Igneous rock	Good. Mixed with NaOH, heated to 550 °C, mixed with metakaolin and Na_2SiO_3	(Tchadjé et al. 2015)
GROSSULAR	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$	Neosilicate/Garnet group		(Xu and Van Deventer 2000)
HALLOYSITE	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	Tubular analogue of kaolinite	Excellent, calcination at 750 °C	(K. J. D. MacKenzie et al. 2007)
HEULANDITE	$(\text{Na}, \text{K}, \text{Ca}, \text{Sr}, \text{Ba})_5(\text{Al}_9\text{Si}_{27})\text{O}_{72} \cdot 26\text{H}_2\text{O}$	Tectosilicate/ Zeolite family		(Xu and Van Deventer 2000)
HORNBLende	$\text{Ca}_2(\text{Mg}, \text{Fe}, \text{Al})_5(\text{Al}, \text{Si})_8\text{O}_{22}(\text{OH})_2$	Inosilicate/ Amphibole group	Mixed with albite	(Bondar et al. 2011)
HYDROXYAPOPHYLLITE	$\text{KCa}_4\text{Si}_8\text{O}_{20}(\text{OH}, \text{F}) \cdot 8\text{H}_2\text{O}$	Framework silicate (Sodalite group)		(Xu and Van Deventer 2000)
ILLITE	$(\text{K}, \text{H}_3\text{O})\text{Al}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{H}_2\text{O},$	Phyllosilicate/ Clay mineral group	Good. Calcination at 750 °C	(Buchwald et al. 2009;

(HYDROMUSCOVITE)	OH_2			Prud'Homme et al. 2011; Xu and Van Deventer 2000)
KAOLINITE	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	Phyllosilicate/ Clay mineral group (1:1 layer lattice aluminosilicate)	Mine waste – up to 70 MPa	(Xu and Van Deventer 2000; Duxson et al. 2005; Linsheng, Wei, and Zongjin 2010; Z. Zhang et al. 2012; Linhua et al. 2009)
KYANITE	Al_2SiO_5	Neosilicate/ Al_2SiO_5 group		(Longhi et al. 2015)
LEPIDOLITE	$\text{K}(\text{Li}, \text{Al})_3(\text{Si}, \text{Al})_4\text{O}_{10}(\text{F}, \text{OH})_2$	Phyllosilicate/ Mica group		(Xu and Van Deventer 2000)
MONTMORILLONITE	$(\text{Na}, \text{Ca})_{0.33}(\text{Al}, \text{Mg})_2(\text{Si}_4\text{O}_{10})$	Phyllosilicate/ Clay mineral group (2:1 layer lattice aluminosilicate)	1 part clay, 0.3 Na-Si 0.05 NaOH 40 MPa	(Mostafa, Mohsen, and El-maghraby 2014; Fernandez, Martirena, and Scrivener 2011)
MUSCOVITE	$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F}, \text{OH})_2$	Phyllosilicate/ Mica group (2:1 layer lattice aluminosilicate)	Excellent, calcination at 950 °C 120 minutes	(Fernando Pacheco-Torgal, Castro-Gomes, and Jalali 2009)
PUMPELLYITE-(FE3+)	$\text{Ca}_2\text{Fe}^{3+}\text{Al}_2(\text{SiO}_4)(\text{Si}_2\text{O}_7)(\text{OH}, \text{O})_2 \cdot \text{H}_2\text{O}$	Garnet group		(Xu and Van Deventer 2000)
PYROPHYLLITE	$\text{Al}_4\text{Si}_6\text{O}_{20}(\text{OH})_4$	Phyllosilicates/ Clay mineral group (2:1 analogue of kaolinite)	Poor, 60 h ball milling (no reactivity after calcination)	(K. J. MacKenzie, Komphanchai, and Vagana 2008)
SILLIMANITE	Al_2SiO_5	Neosilicate/ Al_2SiO_5 group		(Xu and Van Deventer 2000)
SMECTITE GROUP		Clay mineral	Good. Calcination at 750 °C	(Buchwald et al. 2009; Ferone et al. 2013)
SODALITE	$\text{Na}_4(\text{Si}_3\text{Al})\text{O}_{12}\text{Cl}$	Tectosilicate/ Feldspathoid family		(Xu and Van Deventer 2000)
SPODUMENE	$\text{LiAlSi}_2\text{O}_6$	Inosilicate/ Sodium pyroxene series		(Xu and Van Deventer 2000)
STILBITE	$\text{NaCa}_4(\text{Si}_{27}\text{Al}_9)\text{O}_{72} \cdot 30\text{H}_2\text{O}$	Framework silicate (Sodalite group)		(Xu and Van Deventer 2000)

What makes the data in Table 2 difficult to analyze and draw any conclusive conclusions is the mixed nature of the raw materials: in most cases, the starting material is not only a single mineral but also a mix of different minerals. Regardless, low reactivity is the bottleneck for most of the minerals on the list above, and some sort of pretreatment is required in all cases.

The most reactive minerals in the list belong to the group of *1:1 layer lattice aluminosilicates*, which consist of repeating tetrahedral silicate sheets and octahedral hydroxide sheets. Some 1:1 layer lattice aluminosilicates, most notably kaolinite, can be made more reactive by simple heat treatment at 750 °C. The reason behind the effectiveness of heat treatments within these aluminosilicates provides clues to requirements for effective pretreatments in general and will be explored in the following section (4.2.1).

4.2. Pretreatments to enhance reactivity in alkali activation

Reactivity of any material in cementitious systems is relative to the available surface area, which in turn is dictated by the particle size distribution (Snellings 2013). To completely react, the surface area of even highly reactive minerals needs to be high, corresponding to average particle size of roughly ten micrometers. In grain sizes therefore fine silt (3.9–62.5 µm) or clay (0.98–3.9 µm) are preferable. Mine tailings are rarely ground finer than 100 µm particle size, and therefore to yield high reactivity, some mechanical treatment may be required.

Several different kinds of pre-treatments increase the reactivity of the raw materials for alkali activation, and in the following chapters thermal, mechanical, thermochemical and chemical pre-treatments are reviewed.

4.2.1. *Thermal pretreatment*

An abundant low-calcium aluminosilicate source, calcined kaolinite, is the most widely used virgin mineral precursor for alkali activation in the scientific literature (Alonso and Palomo 2001; Bell, Driemeyer, and Kriven 2009; Provis and van Deventer 2014). The reason behind the widespread use is the relatively high solubility of aluminum after calcination at 750 °C (in this context 'solubility' means selective solubility of Al at pH 13 after 24 hours). The tremendously increased solubility of aluminum stems from the coordination of aluminum with hydroxyl groups; at elevated temperatures hydroxyl groups migrate from the layered clay structure and leave the remaining aluminum atoms frustrated and reactive. During thermal treatment, aluminum coordination is changed from 6-fold to a mixture of 4, 5 and 6-fold, which has been shown to increase reactivity (Provis and Van Deventer 2009, 311). Following similar line of reasoning heat treatments have been successfully used in the literature with other aluminosilicate minerals where aluminum is bound to OH-groups.

On the contrary, the aluminum in 2:1 (in contrast to 1:1) layer lattice aluminosilicates is coordinated primarily to silicon and such increase in solubility is not expected by mere heat treatment. Indeed, MacKenzie et al. (2008) postulated that 2:1 layer lattice aluminosilicates do not readily react to form geopolymer after heat treatment.

There are some exceptions that are reported in the literature to this rule: Pacheco-Torgal et al. (2010) have successfully used muscovite, a 2:1 layer lattice aluminosilicate, as an excellent precursor for geopolymers, suggesting relatively high solubility of aluminum. This contradiction may be due to the differences in the degree of substitution between the tetrahedral and octahedral layers as later argued by MacKenzie in a book edited by Provis and Van Deventer (2009, 299). Kaolinite is an often-found impurity in mine tailings, and some of the reactivity seen in by Pacheco-Torgal et al. (2010) could be due to kaolinite, as its source was not thoroughly analyzed.

Heat pretreatment provides a good starting point for increasing the reactivity of any aluminosilicate mineral towards alkali activation, as illustrated by McIntosh et al. (2015), but it will fall short more often than not. The following chapters review additional pretreatment methods.

4.2.2. *Mechanical pretreatments*

In some cases, it is possible that even though calcination leads to dehydroxylation and significant changes in aluminum coordination, the material does not form a viable geopolymer precursor. Such is the case with pyrophyllite, a 2:1 layer lattice aluminosilicate. Different pre-treatment have to be then employed, and MacKenzie et al. (2008) were successful at utilizing mechanical pretreatment to yield a viable geopolymer precursor from it. The mode of action in mechanical treatment is thought to be due to two separate factors: 1) increased surface area due to smaller particles size, and perhaps more importantly 2) reduction of crystalline size and increase in the amount of amorphous material (Welham and Llewellyn 1998; Baláž et al. 2013). In the case of pyrophyllite, the required pretreatment was quite severe (ball milling for 60 h or alternatively vibro milling for 15 min), and therefore mechanical activation alone may be too energy-intensive and not feasible in the large scale.

4.2.3. *Thermochemical treatments*

Different chemical (acid and basic) and thermochemical treatments have shown promise in ability to activate the precursor materials to enhance solubility. In a recent work of Feng et al. (2012), heated albite in the presence of sodium hydroxide producing one-part geopolymer precursors. The treatment consisted of adding 50% of NaOH to albite powder, and heating the mixture to 1000 °C. The heat treatment broke down the albite structure, Si and Al lost their crystalline ordering and new amorphous phases were created

(Feng, Provis, and van Deventer 2012). A similar approach was taken by Tchadjié et al. (2015) in order to utilize granite powder waste as a geopolymer precursor, mixed with metakaolin (60/40). According to their results, the reactivity of the granite powder increased with increasing amount of Na_2O up to 60% by weight, Figure 4.

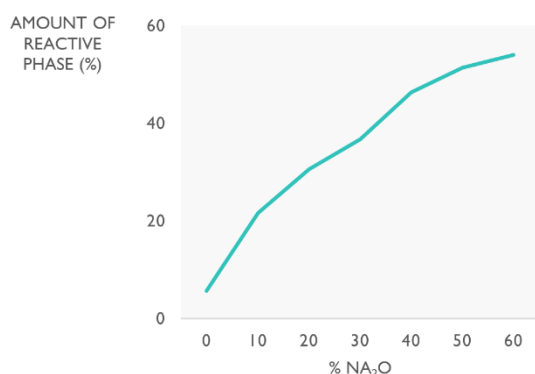


Figure 4: Increasing reactivity of granite powder after heat treatment with varying amounts of NaOH. Data from (Tchadjié et al. 2015).

The so-called fusion process was described as follows: the materials were mixed, heated to 550 °C with 1 °C/min heating procedure and held at the temperature for 2 h. Sample was cooled, crushed and geopolymerized using a Na_2SiO_3 solution with 1.2:1 activator to binder ratio, and an aggregate to binder ratio of 2.75:1. The highest compressive strength, 40.5 MPa, was achieved by adding 40% Na_2O of the raw material. Using a similar approach one-part geopolymer mixes have been recently reported with red mud (up to 10 MPa strength after 7 days of curing) (Ke et al. 2015), and low quality kaolinite (Peng et al. 2014).

These examples of recent works highlight the potential of the alkali-thermal treatment, which may prove highly applicable in alkali activating a wide variety of different aluminosilicate mine tailings. More research is needed in this area to extend the treatment to wider set of aluminosilicate minerals, and to combat the increased water solubility of the final material and problems with durability that have been reported on some mixes (Peng et al. 2014). Too high content of sodium or potassium leads to atmospheric carbonation; the required Na/Al –ratio for adequate charge balancing is 1:1, while the Na/Al -ratios used in the studies cited above are well above that (up to 9.8).

A similar thermal pretreatment is offered by the 'glass route', which offers a step toward a pretreatment method that works irrespective of the mineralogy, based on the chemical oxide composition instead. In order to yield an alkali-soluble precursor, oxide compositions can be designed to produce alkali-soluble glass – this methodology has also been recently applied in low and high-calcium aluminosilicate precursor glasses (Ruiz-Santaquiteria, Fernández-Jiménez, and Palomo 2016). Investigations have concentrated on aluminosilicate and calcium aluminosilicate glasses, where alkali oxides can be used as fluxes to reduce melting temperature. These oxide glass systems share resemblance to alkali-activation of metallurgical slags, which has over century-long history, and therefore has great potential in sustainable construction applications.

4.2.4. Chemical pretreatments

Despite some positive results, little work has been done on chemical pretreatment of aluminosilicate minerals in order to increase their reactivity in alkali activation. Most promising account has been described by MacKenzie et al. (2007); after alkaline pretreatment and alkali activation halloysite clay minerals, a 1:1-layer-lattice aluminosilicate, was converted into a promising albeit crystalline precursor. Pretreatment in solution consisting of 0.1 M NaOH resulted in conversion to crystalline hydrated zeolite LTA ($\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48-27}\text{H}_2\text{O}$) starting at 3 hours, accompanied by a significant amount of tetrahedral aluminum

modified from the originally octahedral state. This pre-treated material facilitated the subsequent geopolymerization reaction, leading to a crystalline product. Being in contact with atmospheric carbon dioxide, the excess alkali turned into sodium aluminosilicate carbonate. Despite the crystalline nature of the end product, this pretreatment process was thought to be the most promising low-energy route of the ones tested, and therefore warrants deeper investigation (K. J. D. MacKenzie et al. 2007).

4.3. Robustness of alkali activation process towards mixed mineralogy mine tailings

In large-scale commercial processes, such as mine tailings recycling, the robustness of the underlying technology is critical, and is therefore the following chapter reviews the scientific literature on alkali activated low-calcium mine tailings (below 10 wt. % CaO). While higher calcium content publications were prevalent, only three examples of low-calcium content alkali-activation of mine tailings was found: tungsten mining side streams (4.3.1), copper mine tailings (4.3.2) and oil sand tailings (4.3.3), out of which oil sand tailings was a review with no experimental results.

4.3.1. Tungsten mining side streams

The most extensive work on alkali-activation of mine tailings has been conducted by Pacheco-Torgal and coworkers recently on muscovite-rich tailings from tungsten mining (F. Pacheco-Torgal and Jalali 2010; 2008c, 2009). The mine waste was calcined at 950 °C for 120 minutes in order to dehydroxylate the mineral, leaving the structure more amorphous. Care had to be taken when cooling the heated material in order to retain the amorphous structure required care in cooling. According to the results, a reaction product consisted of one new crystalline phase, phlogopite.

Pacheco-Torgal et al. (2008b) have shown that calcined muscovite-rich mine tailing is an excellent alkali-activation precursor with NaOH activation ($H_2O/Na_2O = 10$) using 5% $Ca(OH)_2$ addition, yielding up to 70 MPa unconfined compressive strength in 54 days. In addition they achieved very high early strength, low water absorption and good adhesion to OPC cement (Fernando Pacheco-Torgal, Castro-Gomes, and Jalali 2008a; F. Pacheco-Torgal, Castro-Gomes, and Jalali 2010).

Castro-Gomes et al. (2012) took advantage of the visual appearance of the coarse tungsten mine waste, and developed an alkali-activated material, which can be used in artistic applications. Building on Castro-Gomes' earlier work, Silva et al. (2010) applied tungsten mine tailings as a source material for alkali-activated aggregates, which they found suitable for water purification application. The pH of the aggregates stabilized to 8 after 24 hours, and compressive strength of the aggregates were decreased by water immersion, but stayed at acceptable level of two mega Pascals after four weeks. The molar ratios of the starting materials yielding the best results were $Na_2O/Al_2O_3 = 0.36$, $SiO_2/Al_2O_3 = 6.9$ and $H_2O/Na_2O = 14.1$. The authors discussed that the strength of the aggregates may increase with lower water amount.

4.3.2. Copper mine tailings

Copper mine tailings consisting of quartz, albite, alkali feldspar (sanidine), and gypsum were successfully used as a geopolymer precursor to make bricks that met the ASTM requirements for severe weather conditions (Ahmari and Zhang 2012). A compressive strength class of 28 MPa was achieved with 15 M NaOH concentration, initial water content of 16%, 0.5 MPa forming pressure, and 90 °C curing temperature. Surprisingly, low-forming pressures resulted in best results in terms of compressive strength (UCS), water absorption and abrasion index (Table 3) presumably due to lost activator solution with higher pressures as discussed by the authors. The pretreatment of the mine tailing consisted of 2 hours of calcination at 700 °C.

Table 3: Abrasion indices for geopolymer bricks prepared from copper mine tailings. Data from (Ahmari and Zhang 2012)

FORMING PRESSURE (MPa)	UCS (MPa)	24 H WATER ABSORPTION (%)	ABRASION INDEX
---------------------------	-----------	------------------------------	-------------------

0.5	28	0.93	0.02
1.5	25	2.18	0.06
3.0	22	2.92	0.09
5.0	21	3.45	0.11
15.0	21	3.15	0.10

4.3.3. *Oil sand tailings*

Oil sand tailings are the last example included here to scope the robustness of geopolymerization. A recent review concentrated on the prospect of using geopolymerization technology on the stabilization of Albertan oil sand tailings, while also covering the mine tailings in general (Rao and Liu 2015). The mineralogy of Albertan oil sand tailings is indeed promising with 40–70 wt% kaolinite, 30–45 wt% illite and 10 wt% mixed layer illite/smectite and residual bitumen content around 1 wt%. They found the prospects promising despite the presence of bitumen and called for systematic studies on the fundamental geopolymerization mechanisms, such as reaction pathways and structure–strength correlations.

The above three examples of low-calcium mine tailings recycling in alkali activated materials were shown in order to scope the robustness of the method, and therefore potential in mine tailings utilization. Perhaps more convincing though is the widespread and commercial application of calcium-rich waste-based raw materials in geopolymers, covered in following section (4.4).

4.4. Track record of geopolymerization in industrial applications

Track record of alkali-activated slag is over a century-long, with first patent on the alkali-activation of blast furnace slag by Whiting (1895). These earlier works up until 1970's utilized high-calcium precursors, therefore yielding hydrated cement phases poorly applicable to ceramic applications. Low-calcium alkali-activation was coined geopolymerization, and commercialized by Joseph Davidovits in the 1970's (Davidovits and Legrand 1977).

Mass adoption of the technology has happened only recently; worldwide AAM market is on the nascent stage, and is expanding rapidly and fueled by the demand for sustainable materials. A geopolymer market study published in 2015 forecasts an exponential growth for the foreseeable future, a cumulative annual growth rate (CAGR) of over 30% (Mordor Intelligence 2015). The sectors covered were buildings, road and pavements, runways, pipes and concrete repair, bridges, tunnel linings, railroad sleepers and “other uses”. The report covers both high and low-calcium alkali-activated materials/geopolymers and it is difficult to assess their contribution, but it shows the industrial relevance of alkali-activated binders. With such wide industry adoption, it is fair to assume that alkali-activation is potentially transferable to industrial practice in low-calcium mine tailing utilization as well, provided that it is financially sustainable.

5. Phosphate bonded ceramics and processing

In addition to alkali-activated geopolymer technology, another chemistry-based manufacturing method for ceramics is phosphate bonding. Chemically bonded phosphate ceramics, or CBPC are the common name for these products. The key difference between GP and CBPC lies in the chemical reactions and conditions required to form solid matter. As described previously in this paper, geopolymer reactions require a source of aluminosilicate and an alkali activator for the polycondensation reaction to occur. Phosphate ceramics, on the other hand, require an acidic phosphate component or phosphoric acid for the complex acid-base reaction to initiate (A. Wagh, 2004). Producing solids through either of these chemical processes offers a route to forming ceramics with little to no requirement for external energy, particularly in the form of heat.

Even though the term geopolymer is sometimes used imprecisely to describe all inorganic chemically bonded solids, including the ones produced from mixture of phosphoric acid and a source

of aluminosilicate (Douiri et al. 2014; Le-ping et al. 2010; L. Liu et al. 2012), this review will limit the use of the term *geopolymerization* exclusively to alkali activated processes. *Phosphate formation* is referring to processes based on acid-base reaction in acidic phosphate solutions and the products to *phosphate ceramics*. This separation is necessary for distinguishing raw material applicability for these two processes, since even though both rely on the rearrangement of soluble species into three-dimensional networks, the solubility of minerals is not equal in both alkaline and acidic solutions.

5.1. Raw materials and synthesis of CBPCs

According to extensive studies gathered by Wagh (2004), CBPCs are best formed from mono- or divalent oxides that show sparse solubility in acidic phosphate solutions. Insufficiently low solubility does not provide enough ions to rearrange into a 3D framework, whereas excessively high solubility results in crystalline precipitates that cannot form a three-dimensional network. The most suitable laboratory-grade raw materials include magnesium oxide (MgO), calcium oxide (CaO) and zinc oxide (ZnO). The mandatory phosphate component can either be in a form of soluble phosphate precursor or dilute phosphoric acid. Formation of solid matter can occur in room temperature if the process is appropriately controlled. By varying the amount of acidic component, the amount and type of oxides as well as additives results in a great variety of different material compositions. (A. Wagh 2004)

In simplest terms, the formation of phosphate ceramics includes dissolution of a base salt in acid, gelation and forming of precipitates, and finally crystallization. In many ways, the process is analogous to producing ceramic structures by the well-known sol-gel synthesis. The key difference is that phosphate forming does not require subsequent heat treatments to finalize the material. Figure 5 is showing a more detailed depiction of reaction steps proposed by Arun Wagh (2004).

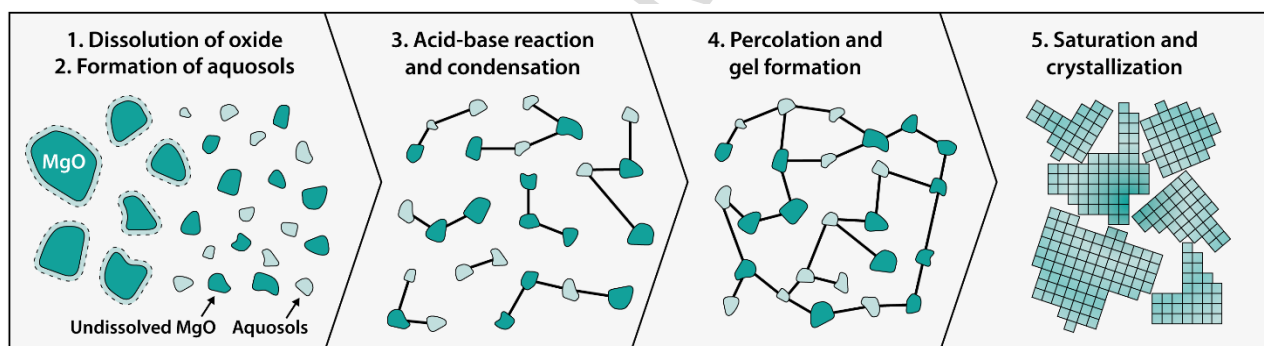


Figure 5: A schematic representation of magnesium phosphate formation in acid phosphate solution, re-drawn based on (A. Wagh 2004).

An important thing to notice is that the formation of phosphate ceramics from sparsely soluble oxides does not completely deplete the raw material. Instead, a significant portion of the primary source is encapsulating as filler into the structure. One could argue, that the presence of primary matter in a phosphate matrix would thus be a sign of the reaction being retarded enough to produce a mechanically stable solid matter.

The chemical bonding of most CBPCs occurs spontaneously by chemical route in ambient temperature. Some reactions, like the one between Wollastonite and acid phosphate for example, are quite exothermic and can result in a very quick setting. Increasing the setting time of such mixtures from minutes to hours can be achieved by chilling the mixture while stirring (H. Colorado et al. 2011). The use of retardants is necessary for reactions that are more aggressive in order to produce a solid ceramic instead of precipitates.

The opposite is true for very sparsely soluble oxides, like aluminum oxide (Al_2O_3) that require heating (150-200°C) of the solution in order to increase the solubility to a level where a ceramic can be formed.

5.2. Pretreatments to adjust reactivity for phosphate bond formation

There is very little research data available on the pretreatments required for minerals to maximize their reactivity for phosphate formation. Most depictions of phosphate-related mineral pretreatments are in fact about phosphate rock tailings, which already have a substantial amount of P_2O_5 . Particle size and chemical composition determine the need for pretreatments of each waste fraction to utilize them in value-added applications. Grinding and wet attrition scrubbing in conjunction with size-separation have been successfully used by Gallala et al. (2016) to produce a concentrate of 29% P_2O_5 content from 13.5% P_2O_5 waste material consisting predominantly of carbonates and fluorapatite.

Heat pretreatments, namely calcination, are usually done for purpose of increasing the reactivity in the raw material. Kaolin can be calcined to produce metakaolin, which in addition to alkali activation, can be used as a precursor for phosphate bonded ceramics as well (Le-ping et al. 2010; Douiri et al. 2014). On the other hand, excessively high solubility and dissolution rate of some laboratory grade oxides such as MgO , CaO and ZnO is undesired, since overly rapid reactions only produce precipitates instead of an extensive 3D-network. The dissolution of MgO powder can be reduced by calcination at 1300°C for 3h, which reduces initial porosity and promotes grain growth, potentially decreasing the amount of available reactive surface area by as much as 99% (A. S. Wagh and Jeong 2003). Preparation of so called phosphoric acid-based geopolymers (Le-ping et al. 2010; Lassinantti Gualtieri, Romagnoli, and Gualtieri 2015) requires transforming kaolin into metakaolin by calcination at 750-800°C to ensure proper reactivity, very similarly to the alkaline geopolymer processing described previously. From mine tailings point of view, initial drying and even calcination may be required in order to improve reactivity. Since the vast majority of the minerals in tailings have fairly low reactivity, the amount of reactive surface area needs to be maximized, which can be achieved by the means of grinding. Unfortunately, both calcination and grinding represent a large amount of embodied energy to be added into the process, making the tailings that require these pretreatments extensively less attractive for utilization in CBPCs.

Some initial heat treatment for mine tailings cannot be avoided due to prolonged storage near or at the mining sites. It has been found, that prolonged storage of primary raw materials in room temperature and atmosphere has a negative effect on compressive strength of CBPCs (H. Colorado, Hiel, and Hahn 2011). The level of reactivity is reduced due to absorption of humidity, a process that can be delayed by storing dried raw material powders in closed containers in low temperature.

5.3. Applicability of phosphate bonding to commonly available minerals in mine tailings

As is the case with alkali-activation, low reactivity of most silicate-based minerals is a challenge for utilizing them for phosphate bonding, though some exceptions (e.g. Wollastonite) exist. In general, mine tailings are less utilized for the phosphate bonding ceramics than for alkali activation. In fact, very little research exists on producing phosphate ceramics of any mining products, be it primary or secondary. Most silicates, while very useful in alkali activation processes, are a challenging group of materials for phosphate formation due to their extremely low solubility in phosphoric acid (A. Wagh 2004). Quartz sand (SiO_2) is commonly used either as inactive aggregate to lower the overall cost of phosphate bonded cements. The poor reactivity of quartz sand with magnesium phosphate was reported to have a negative effect on compressive strength and ageing properties of a phosphate cement (Li, Shi, and Li 2016). Examples of moderately reactive silicates include Wollastonite (CaSiO_3) and tricalcium silicate (Ca_3SiO_5), the former being a potential raw material for structural applications (H. Colorado et al. 2011; H. A. Colorado, Wang, and Yang 2015) and the latter having added biofunctionality when mixed with magnesium phosphate to produce apatite-like structures (W. Liu et al. 2015).

Most frequently used raw materials encountered in publications regarding phosphate synthesis are either derivatives of commercially available mixtures of phosphate binders, or alternatively, soluble acid phosphate salts that are meticulously synthesized from high-grade hydroxides or carbonates through reacting them with hydrogen- or ammonium phosphate salts. Most novel structures with specific stoichiometry are synthesized as coatings or particles in low quantities. On the other hand, in the field of waste management and structural composites, processing is conducted in very robust way and very little emphasis is put on purity of raw materials.

Even though the most widely used phosphate ceramic precursors are few, apatites and monopotassium phosphate (MKP) being the most common, a myriad of different mineral structures can be produced by phosphate forming reaction. This is due to the fact that phosphate formation can have several intermediary products before consolidating into a non-soluble ceramic. The final form of reaction products depends heavily on reaction kinetics and the chemical composition of solid raw materials. Table 4 presents a non-exhaustive collection of phosphate-based minerals found in different applications. Literature examples of precursors and formation processes for the certain applications are also included.

Table 4: Phosphate mineral structures found in ceramic applications

MINERAL	BASE FORMULA	LITERATURE EXAMPLES OF PRECURSORS AND FORMATION PROCESS	APPLICATION
HYDROXYAPATITE	$\text{Ca}_5(\text{PO}_4)_3\cdot\text{OH}$	Producing $\text{Ca}_{(10-x)}\text{B}_x(\text{PO}_4)_6(\text{OH})_2$ by sol-gel method and calcination using $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$ and H_3BO_3 (AlHammad 2016)	Bioceramic
CHLOROAPATITE	$\text{Ca}_5(\text{PO}_4)_3\cdot\text{Cl}$	Producing $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ from $\text{Ca}(\text{OH})_2$, $\text{NH}_4\text{H}_2\text{PO}_4$ and NH_4Cl by solid state reaction in elevated temperature (Jena et al. 2012)	Waste management
BRUSHITE	$\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$	Producing $\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$ by reacting wollastonite (CaSiO_3) with dilute phosphoric acid (H_3PO_4) in room temperature (H. Colorado et al. 2011; H. A. Colorado, Wang, and Yang 2015)	Structural materials, Composites
CARBONATE APATITE	$\text{Ca}_5(\text{PO}_4)_3\cdot\text{CO}_3$	Producing $\text{Ca}_5(\text{PO}_4)_3\cdot\text{CO}_3$ by reacting calcium carbonate in phosphoric acid solution under elevated pressure at 80°C (Pham Minh et al. 2013)	Porous bioceramic
HOPEITE	$\text{Zn}_3(\text{PO}_4)_2\cdot 4\text{H}_2\text{O}$	Preparation of $\text{Zn}_3(\text{PO}_4)_2\cdot 4\text{H}_2\text{O}$ by double decomposition of Na_3PO_4 with ZnCl_2 in room temperature (Parhi et al. 2008)	Bioceramic
HYDROXYPYROMORPHITE	$\text{Pb}_5(\text{PO}_4)_3\cdot\text{OH}$	Formation of $\text{Pb}_5(\text{PO}_4)_3\cdot\text{OH}$ by reaction of soluble Pb-species in soil with phosphate (Sanderson et al. 2015)	Waste management
CHLOROPYROMORPHITE	$\text{Pb}_5(\text{PO}_4)_3\cdot\text{Cl}$	Formation of $\text{Pb}_5(\text{PO}_4)_3\cdot\text{Cl}$ by reaction of cerussite (PbCO_3) and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\cdot\text{OH}$) in a solution at low pH (A. Wagh 2004)	Waste management
FLUOROPYROMORPHITE	$\text{Pb}_5(\text{PO}_4)_3\cdot\text{F}$	Formation of $\text{Pb}_{10}(\text{PO}_4)_6\text{F}_2$ by reaction of fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\cdot\text{F}$) derived from phosphate rock with soluble Pb-species (Cao et al. 2004)	Waste management
STRUVITE	$\text{Mg}(\text{NH}_4)\text{PO}_4\cdot n\text{H}_2\text{O}$	Producing $\text{Mg}(\text{NH}_4)\text{PO}_4\cdot n\text{H}_2\text{O}$ by reacting magnesium oxide (MgO) with monoammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) in a solution (Soudée and Péra 2000)	Structural materials
K-STRUVITE	$\text{MgKPO}_4\cdot n\text{H}_2\text{O}$	Producing $\text{MgKPO}_4\cdot n\text{H}_2\text{O}$ by reacting magnesium oxide (MgO) with monopotassium phosphate (KH_2PO_4) (Morales et al. 2015; Formosa et al. 2012; D. Zheng et al. 2016; A. Wang et al. 2013)	Structural materials, Composites
(MG, CS)-STRUVITE	$\text{MgCsPO}_4\cdot 6\text{H}_2\text{O}$	Formation of $\text{MgCsPO}_4\cdot 6\text{H}_2\text{O}$ by reacting cesium chloride (CsCl), magnesium oxide (MgO) and monopotassium phosphate (KH_2PO_4) in water solution (A. S. Wagh et al. 2016)	Waste management

Majority of the listed mineral structures are practically insoluble, stable products of reacting soluble phosphate salts with sparsely soluble oxides, carbonates and hydroxides in low-pH solutions. However, many of the listed minerals have readily soluble intermediate products or are themselves sparsely soluble, which can be further exploited to produce different, often less soluble structures (e.g. transformation of hydroxyapatite into hydroxypyromorphite, a deliberate product of time-consuming ion exchange process that takes place in soil improvement applications). Given high enough purity, some moderately soluble intermediate products (e.g. magnesium dihydrogen phosphate, $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$) can be utilized in producing even higher-grade materials that have high chemical stability and properties approaching those of engineering ceramics. The formation of desired (or indeed, undesired) precipitates depends heavily on raw material ratio, liquid-to-solid ratio, and pH of a solution. (A. Wagh 2004; A. J. Wang et al. 2013)

5.4. Robustness of phosphate bonding towards unwanted components in the raw materials

As a cementitious process, phosphate bonding is flexible in terms of different filler shapes and chemistries. Chemically bonded phosphate ceramics can be tailored to facilitate considerable amounts of waste matter into their bulk. This applies to both hazardous waste and benign waste, with the distinction that non-harmful waste does not need to be fully immobilized, and thus greater percentage of matter can be incorporated into the matrix. Studies on magnesium phosphate cements have shown that using even a high amount of low-grade raw material (MgO) in conjunction with high-purity one (monopotassium phosphate, MKP, KH_2PO_4) can result in very good physical properties (Formosa et al. 2012; Morales et al. 2015). As with all the other cementitious processes, the addition of inert aggregates can reduce costs. There are, however, unique aspects to phosphate bonding that separates it from alkaline processes. Near-neutral pH (7) of some CBPCs in their solidified form - compared to Portland cement (pH 12) - widens the choice for potential reinforcement particles/fibres, e.g. E-glass, which corrodes under basic conditions. Additionally, the combination of chemical neutrality with relatively low processing temperatures in the phosphate bonding, natural fiber composites are also a real possibility (Donahue and Aro 2010).

Producing a mechanically satisfying composite microstructure does not necessarily require several different raw materials, as demonstrated by Colorado et al. (2011), where mixing wollastonite with phosphoric acid produced a calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) matrix surrounding inclusions of silica (SiO_2), primary wollastonite (CaSiO_3) and brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). Such multiphase structures can be beneficial in load bearing structures, where the increase in fracture toughness due to crack deflection can translate into higher fracture strength. Incorporation of reinforcement materials can further enhance the mechanical properties. In a later study by Colorado and Singh (2014), a similarly diverse composite structure consisting of magnesium phosphate ($\text{Mg}_3(\text{PO}_4)_2$) and several types of sodium phosphates (NaMgPO_4 , Na_3PO_4 , $\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$, NaAlPO_4) was produced by reacting type C fly ash in a water-based slurry containing anhydrous monobasic sodium phosphate (NaH_2PO_4) and calcined magnesium oxide (MgO). Li et al. (2016) report, that the addition of type F fly ash can increase water- and salt resistance of magnesium phosphate cement without sacrificing ultimate compressive strength. This compatibility with fly ash is a telling sign of robustness of phosphate formation towards impurities and compositional variation of raw material. Furthermore, trace amounts of heavy metals commonly present in fly ash are not necessarily a hindrance, since the capability of phosphate cements to immobilize harmful waste is widely researched and well demonstrated (see section 5.5).

As was discussed earlier, the dissolution rate of most (tailing) minerals is insufficient for proper formation of CBPCs. However, some laboratory grade oxides (MgO, CaO, ZnO) have excessively fast and exothermic reactivity in phosphoric acid solutions. Knowledge about retardation of phosphate formation is useful in controlling conventional phosphate cement processes (Ca-P, Zn-P, Mg-P), as well as identifying potential deleterious substances in a tailing fraction. In simplest terms, retarding a CBPC reaction would require severe restriction of oxide dissolution into acidic phosphate solution. Dissolution of precursors in the initial

stages of acid-base reaction cycle requires low pH. Exact range of pH depends primarily on precursor setting, despite of the fact that lower pH (< 6) is beneficial. Thus, an excess of alkaline substance in a phosphate solution can retard, and prevent phosphate formation. It is good to remember, however, that sparsely soluble alkaline oxides are a requisite component of CBPC formation and do not retard the reaction per se. Effective retarding of the reaction by alkalinity requires an alkaline starting solution that prevents initial oxide dissolution. Deliberate retardation of oxide dissolution, especially in the case of fine MgO powders is necessary, and commonly achieved by a small (0.05%-0.5%) addition of boric acid (H_3BO_3) (A. S. Wagh and Jeong 2003; Donahue and Aro 2010; Formosa et al. 2012). The origin of this retardation effect is the temporary coating of lünebergite ($\text{Mg}_3\text{B}_2(\text{PO}_4)_2(\text{OH})_6 \cdot 6\text{H}_2\text{O}$) that inhibits the dissolution of oxide particles, until the pH of a mixture rises and the coating itself is dissolved, allowing dissolution to continue.

5.5. Track record of phosphate bonding in industrial applications

Phosphate bonding has been extensively studied for encapsulation of contaminant metals in waste matter (Hafsteinsdóttir et al. 2015). Notable studies include stabilization of mercury (Randall 2003) and lead (Ibrahim, Sibak, and Abadir 2011) using MKP binder (a mixture of calcined magnesium oxide and monopotassium phosphate) and detoxification of lead-loaded industrial solid waste (Ioannidis and Zouboulis 2003) by the addition of either natural fluorapatite or synthetic hydroxyapatite. Some studies explore the possibility of encapsulating nuclear waste (Pinheiro et al. 2011). In general, these applications take advantage of insolubility of phosphate ceramics in groundwater, as well as the fact that solid material with relatively high volume fraction of aggregate can be produced by this method. Supposedly, volatilization is not a risk, since the final form of the waste composite is achieved chemically at low temperatures. The waste fraction needs to be in micro scale, preferably liquid or a powder with particle size ranging from 4 to 75 microns. (Randall 2003)

The immobilization by phosphate reactions can be achieved by two mechanisms: through chemical bonding to an already immobile matrix, or chemical conversion of soluble waste to an insoluble, immobile species. In the latter case, the resulting material composition will include mineralogical structures in which phosphate mineral exchanges cations with water-soluble contaminants. For example, reaction of hydroxyapatite with lead carbonate (cerussite) in low pH solution results in chloropyromorphite, where calcium ions are substituted by lead (A. Wagh 2004). The long term stability of pyromorphites in soil, however, requires further investigations (Sanderson et al. 2015; Venäläinen 2011). Species of phosphate (pyromorphites) formed in these processes are often sparsely soluble, and thus hardly immobilize the lead completely.

In addition to encapsulating harmful waste, the other aspect of waste management is to repurpose benign waste as raw material for new solid products. The focus of this review is on recycling benign waste, though it is clear that the technologies discussed here are highly capable of incorporating some harmful species as well.

One prominent field of phosphate research is bio ceramics, where phosphate formation is frequently used for producing structures resembling bone tissue (Denry and Kuhn 2015; He et al. 2008). Different types of apatite and calcium phosphates are the most widely used varieties of these materials. Historically, CBPCs have strong basis in tooth prosthesis applications, where zinc phosphates were extensively researched and are still used commercially as luting agents and base cements for dental restoration due to their rapid curing. The viability of utilizing mine tailings for bio ceramic production by phosphate formation is questionable, and is out of scope of this review, though advances made in the medical field regarding phosphate synthesis should not be overlooked.

5.6. Beneficiation of secondary phosphate

Phosphorus is a scarce and non-renewable raw material with the main use as fertilizer in agriculture. The main product extracted from phosphate ore is orthophosphoric acid; H_3PO_4 , a necessary component in producing commercially available acid phosphates that can be further reacted into phosphate ceramics by mixing them with appropriate oxides in aqueous mixtures. However, using primary phosphate rock derivatives like phosphoric acid partially defeats the purpose of effectively utilizing mine tailings or other secondary raw materials. The addition of phosphate rock to the list of critical elements for EU in 2014 drives policies promoting sustainable phosphorus management and research, as well as recovery and recycling regulations. Though the mined phosphorus is not consumed but rather eventually dissipated into oceans, biogenic processes that concentrate the minerals occur over geological time, creating a long break in otherwise almost closed phosphorus cycle (Mew 2016). Thus, sustainable source of phosphorus is an important consideration, especially for value-adding processes envisioned in this paper. Beneficiation of secondary phosphate sources is the obvious route to explore when minimal burden on primary sources is emphasized.

Utilizing low-grade ore becomes more relevant as technology advances and primary sources with high P_2O_5 content become depleted. Beneficiation of low-grade phosphate ore (Gallala, Saïdi, et al. 2016) and reuse of phosphate waste (Birken et al. 2016; Hakkou, Benzaazoua, and Bussière 2016; Loutou et al. 2013) have become highly researched topics. The most viable high-volume applications of low-phosphate side streams are aggregates, brick manufacturing, pottery and improving agricultural soils (Ahmed and Abdel-zaher 2014; Negm and Abouzeid 2008). Waste with higher phosphate content can be treated to get high-grade marketable concentrate (Gallala, Herchi, et al. 2016).

According to Zheng et al. (2015), the effects of phosphate rock consisting of dolomite ($\text{CaMg}(\text{CO}_3)_2$), apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) and quartz (SiO_2) on properties of Portland cement are similar to using plain quartz, where yield stress and water demand decrease and setting time increases due to dilution of the mixture. Given the status of a critical element, the utilization of phosphate rock waste matter with high (>10%) content of P_2O_5 as plain non-reactive aggregate should be avoided. Instead, attempts could be made to treat the waste to become a reactive part of phosphate bonding in cementitious mixtures.

6. Environmental and sustainability implications and future concerns

Sustainability of mining tailings management rests on effective metal and/or industrial mineral refinement (with economically acceptable cut offs), deployment of capable technologies in minimization of impacts arising from the waste disposal, but also utilization of the tailings as construction materials in roads if stated as inert. Tailings can be used not only as a feedstock for producing a product such as recovered minerals and metals (e.g. Co) and metalloids (e.g. Sb) but also as materials for chemically bonded ceramics, as shown in the previous chapters. The utilization of tailings provides environmental benefits by diverting them from landfill, and geopolymers are able to incorporate a higher fraction of waste material than is possible using blended cements, and with lower CO_2 emissions where tailings are reactive enough. Furthermore, geopolymer technology provides an opportunity to immobilize heavy metals of tailings by incorporating them into the geopolymeric network or by physical encapsulation (L. Zheng, Wang, and Shi 2010; El-Eswed et al. 2015).

Finding the most sustainable approach to mine tailing management is not always straightforward. Adiansyah et al. proposed a guiding framework that takes into account the difficulties in finding the appropriate technologies that consider sustainable development in tailings management (2015). The framework provides detailed steps to determine mine tailings disposal options, which will aid in reaching environmental sustainability without jeopardizing the economical. As a final note they call for future

research to elaborate on the potential of tailings reuse within the industrial symbiosis concept as it will not only reduce the volume of tailings but also provide tools to be used within the proposed framework.

Chemically bonded ceramics is one of such tools, and therefore there is a real need for the type of research reviewed here. However, the environmental sustainability of a process such as alkali-activation of mine tailings will need to be considered case by case as the results will depend on the details; the global warming potential of geopolymers compared to ordinary Portland cement can range from 96% reduction (Guillaume Habert and Ouellet-Plamondon 2016) to 20% increase (G. Habert, d'Espinose de Lacaillerie, and Roussel 2011) depending on the specifics of the approach.

Utilization in construction materials, enabled by alkali activation, is one specific example (P. Duxson et al. 2007; Ahmari and Zhang 2012, 2013). When applied to tailings utilization, high temperature pretreatments may be necessary, which will somewhat lower the advantage over OPC, compared to slag-based geopolymers. Another critical factor determining the environmental footprint of a geopolymer is the activator dose when silicate or hydroxide activators are used, e.g. Cl_2 (Chlorine gas) emissions from the NaOH production via chloralkali process (P. Duxson et al. 2007).

Reactivity increase gained by pre-treatments can be small and processes energy-intensive, and therefore is not always justifiable. One example of high reactivity increase was recently published on phlogopite ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$), that is almost inert in its original form (1% aluminum dissolution in 6M NaOH, (Sreenivasan et al. 2017). After melting, quenching and grinding the phlogopite separated from mine tailings, its alkali-reactivity was radically increased from 1% to 40%. The process can be thought to be energy-intensive but justifiable depending on the end use; by using the prepared glass as a supplementary cementitious material (SCM), formation of carbon-binding reaction products is possible (for example $\text{MgCO}_3 \cdot \text{H}_2\text{O}$), opening the possibility for carbon-sequestering concrete. Therefore, relatively costly and energy-consuming pre-treatments may be justified if the material can be used to substitute an equally energy-intensive product with potentially superior qualities.

7. Discussion

Tailings dam breaches from conventional dams account for most of the environmental incidents related to extractive industries (Edraki et al. 2014), and risks are further increasing due to production of larger volumes of tailings dictated by increased production volumes and poorer ore grades. This, together with increased stakeholder awareness is prompting increased scrutiny of tailings storage facilities from both society and regulators. As a consequence, there is increasing interest towards advanced tailings management methods, including thickened tailings, paste and dry stacking solutions, in order to mitigate risks related to conventional tailings management, social responsibility, environmental impact and economics. (Suvio et al. 2016)

From the economical point of view, this increase in dry-stacking will significantly increase the utilization potential of the stored tailings. The economic value of well-characterized and sorted mineral stacks is naturally much higher than that of unpredictable tailings ponds with unknown content. Depending on the mineralogy of ore deposits, the content of tailing wastes in active and planned mines should value their by-products as a mineral resource suitable for raw materials of ceramics. Tailings utilization could be an important phase before decommissioning the facility. (Adiansyah et al. 2015; Edraki et al. 2014; Kauppila et al. 2011)

To this end, an integrated recycling system has been proposed for the tailings, including a decontamination step for mineral fraction that can be then recycled in secondary applications. The recycling system would be based on the economic principle that the costs of excavating, transporting, milling and decontamination of the tailings are spread over a number of different processes, all of which provide an additional income or cost saving to the overall mining operation, and eliminating the need for costly tailings pond rehabilitation.

(Edraki et al. 2014) Similarities with this line of thinking can be seen with the pulp and paper industry that went through a transformation of a similar kind in the past 30 years, first closing the process water loop and then evolving into integrated bio-product mills.

One key issue for utilizing tailings waste for raw materials of industrial ceramics is the mixed mineral content. The most reactive aluminosilicates belong to the 1:1 layer lattice aluminosilicates such as kaolinite, which rarely occur in tailings when exploiting Proterozoic metamorphic metal ore deposits but they may exist in tailings from younger sedimentary ore deposits (Heikkinen and Räsänen 2009; Parviainen 2009). However, the potential substitution of the tetrahedral sites by aluminum during heat treatment in muscovite, 2:1 layer lattice aluminosilicate, may support the utilization of tailings poor in clay minerals.

The alkali-solubility of several aluminosilicates in tailings is poor and it may need several pretreatments in geopolymer processing. Overall, tailings with minerals bearing hydroxyl groups are potentially suitable for alkali-activation after calcination. For non-hydroxyl-bearing minerals there are countless possible variations in pre-processing combinations, which can assist using tailings wastes for both geopolymerization and phosphate bonding. Most common combination for increasing the reactivity of minerals is heat treatment (drying, calcination) followed by mechanical grinding for the purpose of increasing reactive surface area or liberating reactive components from inert components (e.g. quartz). Unfortunately, grinding is a highly energy-intensive process, as indicated by the fact that it can encompass over 80% of comminution (particle size reduction) in mining (Jeswiet and Szekeres 2016) and contributes to 32% of total energy consumed by mining globally (Holmberg et al. 2017). Consequently, large-scale utilization of fractions that require extensive grinding is less appealing by default. More exact effect of grinding and other pre-treatments on process viability needs to be assessed case by case, however. One approach for that has been put forward by Adiansyah et al., who proposed a guiding framework that can be used in order to take into account available tailings disposal options with their merits and disadvantages (2015).

Screening for suitable pretreatment methods is a little-explored subject, which deserves more attention; as more knowledge is gained on optimal pretreatments apart from simple calcination, the list of suitable minerals for producing CBCs will grow as well. Effective selection of appropriate treatments can only be done when the reactive components in a tailing fraction are identified. Tools for this identification include XRD, XRF, IR-spectroscopy and TGA, especially when used concurrently (Birken et al. 2016). Additionally, the basic phenomena behind overall reactivity of minerals need to be understood in more detail than what the literature reveals. For example, there is still no agreement on the mechanism of dissolution of the simplest of minerals, despite recent exiting advances (Cailleteau et al. 2008; Pustovgar et al. 2016).

Due to impurities and relatively coarse particle size of some tailings, not all processing methods mentioned in this review are viable without further milling and treatment of raw materials. Small particle size is necessary for achieving sufficient reactive surface area, which is a key process variable in all applications of chemically bonded ceramics. The rate of dissolution is directly proportional to surface area, and therefore small particle size (<10 µm) will assure adequate dissolution of sparsely soluble or nearly insoluble oxides of mineral grains in order to have enough ions for rearranging into 3-dimensional networks. Given overall suitable range of pH, cementitious processes based on chemical bonding are, in general, very robust towards impurities. This also translates into capability to envelop large amounts of filler matter, be it reinforcement particles for improving mechanical properties or waste matter for immobilization of contaminant metals. Complete dissolution of precursors is not required, since often chemically bonded ceramics form a composite material between the reacted, solidified matrix and non-reacted mineral grains. Multi-phase structures can even have a positive effect on mechanical properties of CBCs.

Some legislative barriers hinder the utilization of mine tailings — while the driving force to make changes is to upgrade mine tailings into profitable by-products, their waste status can be a major hindrance for

recycling. There are examples when reasonable ways of recycling tailings have been found, but their waste status is preventing implementation of reuse on a wider scale. Investigating mine tailings' properties in order to change the status of benign mine tailings' from waste to reusable material is feasible and attainable goal for future.

In addition to legislation, the highest barrier to utilization may be due to the mode of storage. For example ultramafic tailings have been known to be a viable raw material for mineral wool production for decades (Marabini et al. 1998), however it is not commonly used. Arguably, therefore, the lack of utilization is not due to mixed mineralogy, but perhaps due the inhomogeneity of the tailings: when stored in wet ponds with process water, the once-homogeneous feed becomes segregated and inhomogeneous. Higher utilization of tailings should then be expected from dry-stacked and paste tailings, especially where mineralogy is constant or predictable.

8. Conclusions

The accumulation of mine tailings from the extraction of mineral presents a large environmental problem worldwide, accounting for roughly 5 to 7 billion tons of tailings, stored in over 3500 lake-size dams around the world (Kossoff et al. 2014; Mudd and Boger 2013). This flow of material can also be seen as a resource, and the extractive industries are being affected by the same shift that has transformed pulp & paper industry; once water-thirsty and polluting pulp mills that produced a single product, pulp for paper, turned into almost waterless bioproduct mills that purify and sell most of their side streams. As shown in this review, even impure silicate minerals present a suitable raw material for chemically bonded ceramics coupled with suitable pre-treatment methods to increase reactivity. Since silicate minerals cover over 90 % of Earth's crust, this utilization presents a tremendous opportunity and may offer a way toward higher utilization of mineral side streams from the extractive industry.

The research data compiled in this study strongly supports the hypothesis of versatility and robustness of alkali-activation and phosphate bonding with heterogeneous secondary raw materials. However, in order to take full advantage of these CBC-methods in utilizing widely variable mine tailings, it is imperative that the reactivity of different minerals present is better understood. In general, it can be stated that majority of mine tailings consist of highly stable and thus insoluble mineral species, which leads to a necessity for pretreatments to increase the potential pool of raw materials. As this review illustrates there is a lack of standardization in research methodology, which should be addressed as the field matures. Energy-intensity of the pre-treatments needs to be taken into account - while sometimes prohibitive, in other cases the end use potential of the treated tailing may justify highly energy-intensive pre-treatments.

Changes in legislation and advances in technology are likely to further increase the utilization level of waste produced by mining industry. The lack of legislative incentive is likely one of the reasons behind the lack of current larger scale mine tailing recycling. Diminishing primary resources of phosphate and the addition of phosphate rock onto the list of critical materials in EU have already generated a wave of studies on beneficiation of high-P content phosphate tailings. Similar effects can be expected elsewhere as regulations on waste management become tighter and emphasis on circular economy grows further.

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10. Glossary

AAM	Alkali activated materials
CBC	Chemically bonded ceramics

CBPC	Chemically bonded phosphate ceramics
C-(N)-A-S-H / C-A-S-H / N-A-S-H / C-S-H	Main binding phases in alkali-activated materials, with cement-chemist notation, where: C = CaO, N = Na ₂ O, A = Al ₂ O ₃ , S = SiO ₂ and H = OH.
Gangue mineral	Minerals of no commercial value
Ionic/covalent bond	Strong electrostatic bonds resulting from sharing or transferring of electrons
IP	Inorganic polymer
MKP	Monopotassium phosphate, KH ₂ PO ₄
OPC	Regular cement (ordinary Portland cement)
Van der Waals forces	Relatively weak electric forces that attract neutral molecules to one another

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