Valorization of Finnish mining tailings for use in the ceramics industry



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Abstract

The present study valorized Finnish mining tailings waste to identify opportunities for the use of ceramics technologies. On the basis of their mineralogical and chemical contents, the five selected tailings wastes represented felsic mining tailings (FMT) rich in quartz and alkali feldspars, mining tailings dominated by Mg- and Fe-bearing minerals (MgFeMT), and mining tailings rich in carbonate minerals (CMT). Preliminary pilot studies indicated that the FMT materials are potential secondary raw materials for mullite-type ceramics. An Al additive was needed, since the Al_2O_3 content of the studied tailings was too low for mullitization. In addition, carbonate-bearing tailings with Ca silicates can be applicable for chemically bonded phosphate ceramic (CBPC) synthesis. Based on a literature review, FMT are viable source materials for the production of geopolymers, but a high initial Si:Al ratio (in quartz-rich FMT) may lead to partial geopolymerization. Preliminary results from the geopolymerization of pre-heated phlogopite mica mixed with metakaolin gave promising findings, with the formation of a geopolymer having good compressive strength. The findings support the viability of MgFeMT materials rich in phlogopite mica for the production of alkali-activated ceramics.

Keywords: Mining tailings, utilization, geopolymer, phosphate ceramics, chemically bonded ceramics, mullitization, sintered bonded ceramics, tailings minerals, mineralogy, geochemistry

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1. Introduction

The utilization of mining tailings, which are at present classified as waste, is a target of growing interest. Tailings are a major waste material, comprising the remains generated from ore processing. In current practice, they are transported in slurry form and deposited in storage impoundments (Kauppila et al., 2011). This storage leads to the occupation of large areas of land, costly construction and maintenance, and potential environmental and ecological risks, e.g. acid mine drainage (Jambor et al., 2003). Therefore, it is important to reduce the risk of environmental contamination by tailings. On the other hand, the need for substitute materials will grow in the future as the amounts of easily exploitable ores, dimension stones, and industrial minerals diminish (e.g. Ahmari & Zhang, 2012; Shreekant et al., 2016).

A common approach is to utilize inert tailings as a construction material at the mining site, including in road construction, as backfill material in underground mines, and as dam support material (Kauppila et al., 2011). Tailings have been investigated and utilized on a minor scale as a building material, to make bricks (Ahmari & Zhang, 2012, 2013; Zhang, 2013), mineral wool (Marabini et al., 1998), and various ceramic products such as glass ceramics (Marabini et al., 1998, Shao et al., 2005, Ye et al., 2015) and geopolymers (Pacheo-Torgal et al., 2008, 2010; Ahmari & Zhang, 2012, 2013).

Chemically bonded ceramics can be thought to share properties with both cements and ceramics and may offer a route to upgrading mine tailings into secondary raw materials (Kinnunen et al., 2018). The technology is based on alkali activation (Duxson et al. 2005) and phosphoric acid treatment (CBPC, chemically-bonded phosphate ceramics; Wagh, 2013). One of the advantages is that the synthesis process does not involve high temperatures, unlike the conventional ceramic route (sintering).

The objective of this study was to develop classification and valorization concepts for mining

tailings, focusing on their reuse as secondary raw materials in ceramics technologies (see Kinnunen et al., 2018). Experimental laboratory work, including chemical reactivity tests, was carried out to probe the viability of the tailings in producing chemically bonded ceramics (alkali-activated, phosphoric acid treated) and reaction sintered (mullitized) ceramics. This article presents the preliminary results from these tests, but it does not evaluate the profitability of utilizing tailings. The study materials, comprising tailings from five mine sites, were selected on the basis of their mineral and chemical contents. The most essential criterion was their nonradioactive and inert characteristics. In addition to these, virgin metakaolin and commercial phlogopite separated from apatite ore flotation was used to simulate the viability of the phlogopite-rich tailings for geopolymerization.

2. Experimental work

2.1 Materials and sampling

The studied materials were sampled from the tailings impoundments of a closed mine (Mätäsvaara molybdenum mine) and four active mines (Table 1). The samples did not represent the whole tailings bed, but only the shallow tailings at one sampling point. Altogether, six samples were taken from the shallow tailings by digging with a shovel. In the calcite-wollastonite mine, the samples were taken from both the coarse and fine-grained tailing phases separately dumped in a pile storage and in the impoundment, respectively (CERAT10). In the other mines, samples were taken from the shallow tailings between the depth of 10 cm and 40 cm, except at the Mo mine, where the sampling depth was from 10 cm to 1 m. Tailings samples of about 2 kg were placed into 5-l plastic bags for basic chemical and mineralogical analyses, and 5-6 liters of tailings samples were collected into 10-l buckets. Altogether, 6 buckets of samples were taken from each site for ceramics studies.

Deposit	Sample ID	Host rock	Deposit-forming processes	References
Siilinjärvi apatite - phlogopite ore	CERAT1	Carbonatite	Magmatic	0'Brien et al., 2015
Pampalo gold ore	CERAT2	Tholeitic metabasalt, sedimentary rocks, mafic schist	Metamorphic, hydrothermal	Sorjonen-Ward et al., 2015
Kinahmi quartz ore	CERAT5	Quartzite	Sedimentary, metamorphic	Lehtinen, 2015
Mätäsvaara Mo ore	CERAT7	Neoarchean granitoids	Metasomatic	Haapala & Rämö, 2015
Ihalainen limestone- wollastonite ore	CERAT10	Limestone	Sedimentary, metamorphic	Lehtinen, 2015

Table 1. Geological settings of the tailings.

Table 2. The composition (% w/w) of phlogopite (MicaFort) and metakaolin (MetaMax). Analyses were conducted with a PANalytical AXiosmAX XRF spectrometer fitted with a rhodium tube having a maximum power rating of 4 kW at the University of Oulu.

Sample	SiO ₂	AI_2O_3	MgO	CaO	Fe_2O_3	K ₂ O	Na ₂ O	F	TiO ₂	Co ₃ O ₄	LOI
MicaFort PD900 (CERAT8)	40.9	9.8	23.8	1.5	9.1	8.6	0.2	0.5	0.2	0.2	5.6
MetaMax	53	44.5	-	-	0.4	0.1	0.3	-	1.4	-	0.3

Furthermore, the following commercial minerals were sampled: phlogopite, a by-product (MicaFort PD900) from the Siilinjärvi apatite mine, and metakaolin, branded MetaMax, from BASF. The commercial phlogopite (sample named CERAT8) was used to simulate Siilinjärvi mine tailings (CERAT1) in heating and alkali activation. Metakaolin refers to the dehydroxylated product of calcination of kaolinite clays at temperatures of around 500–800 °C. It was used as the base mineral in geopolymerization. The compositions of phlogopite and metakaolin are presented in Table 2.

2.2 Mineralogical analyses of tailings samples

For the mineralogical characterization, vertical polished 25-mm (ECD) epoxy mounts were prepared from the air-dried tailings samples. The

mounts were coated with graphite to achieve conductivity. The characterization included the identification and quantification of mineral phases using Oxford Instruments INCA Feature software. Mineral identification was based on GTK's internal mineral database. From 6000 to 12 000 individual mineral particles were analyzed from each sample to determine the modal mineralogical composition. The mineral composition was analyzed using a JEOL JSM 7100F Schottky field emission scanning electron microscope (FE-SEM) attached to an Oxford Instruments EDS spectrometer X-Max 80 mm² (SDD) at the Research Laboratory of the Geological Survey of Finland in Espoo. The analytical conditions were as follows: high vacuum mode, a COMPO back-scattered signal (BSE), 20 kV accelerating voltage, and 0.5 nA probe current.

The mineral identification was based on matching of the numerical elemental composition

converted from the EDS spectra to GTK's internal mineral database. EDS analyses are semiquantitative and the results are normalized to 100%. The limits of detection typically range from 0.3 to 0.5 wt.% per element. Exact identification of phases is not always possible based on the EDS data. Minerals/phases that contain C, Cl, OH- or H₂Ogroups, Be, or lighter elements cannot be analyzed. The beam is typically generated over an area of 3 μ m in diameter. Grains that are smaller than this cannot be analyzed precisely.

2.3 Chemical analysis of tailing samples

The total concentrations of elements in the tailings samples were determined with a Panalytical AXIOS PW4400 fitted with a rhodium tube having a maximum power rating of 3 kW. For chemical leach analysis, fresh tailings samples were freeze-dried and then sieved to <2mm grain size. Leaching with Aqua regia leach, a mixture of HNO₃ and HCl (1:3), was used to determine the content of mica and the clay mineral fraction and its acid extractable elements concentrations (Niskavaara, 1995). Aqua regia entirely digests trioctahedral micas, clay minerals, sulfides, saline minerals, and secondary precipitates, and some Mg and Ca silicates such as serpentine and sphene (Doležal et al., 1968; Räisänen et al., 1992). Element concentrations in the leachates were measured with inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). The sample treatments and ICP and XRF determinations were performed in the accredited laboratory of Labtium Oy (FINAS T025, EN ISO/IEC 17025).

2.4 Methods in geopolymerization

Thermal pretreatment was performed to improve the viability of phlogopite (MicaFort PD900, CERAT8) as a precursor for alkali activation. Earlier studies based on alkaline solubility tests have indicated that phlogopite is practically inert for alkali activation, and its activity could be significantly improved by thermal treatment at 1600 °C (Sreenivasan et al., 2017). The phlogopite sample in a corundum crucible (40-g batch size) was placed inside a Nabertherm high-temperature furnace (HT 08/18) and rapidly heated (20 °C/ min) to 1600 °C. It was held at the highest temperature for 2 hours. After the holding time, the melt was subjected to rapid cooling over a watercooled copper plate. The heated sample was named CERAT8_T. The experiments were performed by H. Sreenivasan, a doctoral student at the University of Oulu, under the guidance of Dr P. Kinnunen and Prof. M. Illikainen.

The alkali dissolution rate test for metakaolin and also for the heated phlogopite was conducted as follows: The sample was mixed with 6M NaOH with a liquid/solid ratio of 450 (v/w) in a polypropylene bottle. During the test, the sample was held at 23 °C for 1 day without stirring. The solution was periodically sampled, and the sampled solution was filtered through 0.45- μ m filter paper. In the next step, the filtrate was acidified with nitric acid to a pH lower than 2 and was subsequently analyzed by ICP to determine the elemental concentrations. Here, we only present the concentrations of Si and Al dissolved in the alkali treatment.

Geopolymers were prepared from metakaolin alone and by mixing metakaolin and the thermally pretreated phlogopite (sample CERA8_T) as precursors (Table 3). Sodium silicate solution was used as an activator. During the preparation of the activating solution, NaOH pellets were first completely dissolved in distilled water, after which fumed silica was added. Sodium hexametaphosphate (1 wt.% of solids) was added as a dispersant. The prepared activating solution was finally stirred for 1 day in order to reach equilibrium before being used for the geopolymer synthesis. The precursors and activating solution were mixed using a high-shear mixer (IKA EUROSTAR 20) at 3000 rpm for 30 minutes. The slurry was then introduced into cylindrical plastic molds (25 mm diameter and 25 mm height) and sealed in plastic bags for curing. The curing process consisted of

Sample ID	Metakaolin (g)	Phlogopite (g)	Water (g)	NaOH (g)	Silica (g)	Curing Conditions
MG40	80	0	60.5	28	30	40 °C for 1 day & RT ¹ for 1 day
MPG40	60	20	60.5	28	30	40 °C for 1 day & RT for 1 day
MPG60	60	20	60.5	28	30	60 °C for 1 day & RT for 1 day
MPG80	60	20	60.5	28	30	80 °C for 1 day & RT for 1 day

Table 3. Formulation of geopolymers. Key: MG = metakaolin geopolymer, MPG40–MPG80 = metakaolin + heated phlogopite geopolymer.

¹RT: Room temperature

one day of curing at slightly elevated temperatures $(40 \,^{\circ}\text{C} \text{ to } 80 \,^{\circ}\text{C})$ followed by one day at room temperature (Table 3).

The compressive strength of the geopolymers was analyzed using a Zwick 100 testing machine employing a loading force of 2.4 kN/s. Mineral transformations were studied with XRD methods before and after the heating and alkali activation treatments. The analysis conditions were as follows: Co K α radiation (K α_1 = 1.78892 Å; K α_2 = 1.79278 Å; K $\alpha_1/K\alpha_2$ = 0.5), a scan rate of 3 °/min between 5 ° and 85 ° (20), and 0.02 °/step. A Rigaku SmartLab 9 kW XRD system was used to record diffraction patterns and "X'pert HighScore Plus" PANalytical software for the mineral identification.

2.5 Methods in phosphate reactivity screening

Preliminary testing of the selected mine tailings for reactivity in phosphoric acid was conducted in the form of static exposure tests, with no stirring of mixtures after initial mixing. The tests were performed by researchers at the University of Tampere. Of the fractions reported in Table 1, six samples in total (from CERAT1 to CERAT10coarse and CERAT10- fine) were exposed to 2.5% orthophosphoric acid (H_3PO_4 , VWR) solution for 24 hours and 1080 hours in closed containers. The liquid to tailings ratio was 1:1.5 g of 2.5% aqueous orthophosphoric acid solution to 5 g of dry tailings. Excess liquid was removed by evaporation at 50 °C in a heat cabin (Termaks, TS 8136) after the acid exposure period.

The shorter (24 h) exposure produced the primary set of samples for observing and identifying rapidly forming crystalline phosphate precipitates. The purpose of this was to establish whether there were reactive, i.e. soluble, components in the tailings fractions under investigation. The secondary (1080 h) set of samples was produced to establish whether long-term changes in mineralogy would occur, since some phosphate-related mineralogical changes occur slowly. Guided by the results from these preliminary investigations, further reactivity testing in 10% H₃PO₄ solution was performed on the two CERAT10 fractions. Additionally, 30 g of the coarse fraction of CERAT10 was mixed with 500 ml of 1.0% and 2.5% H_3PO_4 for 60 minutes to achieve a higher dissolution of soluble species. In the results section, this is referred to as washing due to excess liquid being subsequently removed from the mixture by sieving as well as drying.

SEM imaging and analysis of phosphate-treated fractions was performed using a Philips XL-30 scanning electron microscope with an EDAX DX 4 EDS analyzer. An X-ray diffractometer (XRD, Empyrean, PANalytical) with a CuKa radiation source and HighScore Plus software was used for the qualitative analysis.

Table 4. Particle-size distributions (wt.%) of mine tailings after jet milling.

Mine tailings	d10 (µm)	d90 (µm)
CERAT2	1.57	12.4
CERAT5	1.09	9.32
CERAT7	1.36	12.1

Table 5. Formulation of sintered ceramics mixtures.

Sample code	Mine tailings	(g)	Al powder (g)	AIO(OH) powder (g)
SIN01	CERAT2	162.5	87.5	-
SIN02	CERAT2	101	-	149
SIN03	CERAT5	101	149	-
SIN04	CERAT5	72	-	178
SIN05	CERAT7	132.5	117.5	-
SIN06	CERAT7	84	-	166

2.6 Methods in reaction sintered ceramics

Tests for sintered bonded ceramics were conducted at the laboratory of VTT. The suitability and reactivity of three mine tailings (CERAT2 from the gold mine, CERAT5 from the quartz mine, and CERAT7 from the Mo mine) as raw material for mullite-based ceramics were investigated with reaction sintering tests. Mine tailings were first ground by jet milling aiming at a particle size of under 10 µm in order to increase the reactivity for sintering (Table 4). Recipes were formulated aiming at a composition of 3:2 mullite (3Al₂O₃·2SiO₂), and two mixtures were prepared from each mine tailings with metallic aluminum and aluminum oxide hydroxide [boehmite, AlO(OH)] powders as aluminium sources (Table 5). Recipes for the mixtures were calculated according to the chemical composition analysis of the mine tailings and by balancing the Si:Al ratio (see Table 7). Aluminum powder was provided by ECKA Granules (average grain size $<17 \mu m$) and aluminum oxide hydroxide by Sasol Germany GmbH (average grain size <0.77 μm).

Before sintering experiments, the samples presented in Table 5 were mixed by milling in

an attrition mill for 30 minutes in an argon atmosphere. Attrition-milled mixtures were then uniaxially compressed to green pellets of 20 x 3 mm in size using approximately 25 MPa pressure. Reaction sintering of the pellets was performed in an ENTECH air chamber furnace in an air atmosphere, and in ambient air pressure. The heating rate was 3.3 °C/min up to 1300 °C, and this temperature was maintained for 3 hours before cooling to room temperature with a cooling rate of 5 °C/min. Qualitative phase analysis was performed for heat-treated products by using an X-ray diffractometer (XRD, Empyrean, PANalytical B.V., ALMELO, Netherlands) with a CuKa radiation source, and analyzed using HighScore Plus software.

3. Results and discussion

3.1 Mineralogical and chemical composition of the tailings

On the basis of mineralogy and geochemistry, the tailings samples were grouped in three types of secondary raw materials with potential for ceramics production (Tables 6 and 7). The groups are felsic mine tailings (FMT) rich in quartz and alkali feldspars, mining tailings predominantly containing Table 6. The main mineral composition of the tailings from metal and industrial mineral production in Finland. The content of alkali feldspars is the sum of albite and K feldspar (mainly orthoclase), the mica content is the sum of trioctahedral (biotite and/or phlogopite) and dioctahedral micas (muscovite), the Mg-Fe silicate content is the sum of amphiboles (e.g. tremolite, hornblende), serpentine and talc, the content of carbonate minerals the sum of calcite and dolomite, and Ca silicate content is the sum of wollastonite and diopside (±clinozoisite). The distribution of grain-size fractions was determined with the sedigraph method by Labtium Oy.

Sample code	Quartz	Alkali feldspar s	K micas	Mg-Fe silicates	Carbonate minerals	Ca silicates	<0.063 mm	<0.02 mm	<0.002 mm
				wt-%				%	
			Felsic m	ining tailings (FM	T)				
CERAT2	10.6	45.6	21.6	3.73	5.87	non	45	16	2.5
CERAT5	76.6	<0.5	17.7	<0.5	non	non	24	11	2.8
CERAT7	39.9	29.2	8.26	<0.5	non	non	9.6	5.1	1.4
		Mining tailir	ngs rich in I	Mg-Fe-bearing mi	nerals (MgFe	MT)			
CERAT1	<0.5	2.38	63.5 ¹⁾	3.75	20.0	non	8.1	4.1	1.1
	Mir	ning tailings	rich in carl	oonate minerals ±	wollastonite	(CMT)			
CERAT10 coarse	5.92	5.26	non	non	17.1	64.1	9.4	4.0	0.8
CERAT10 fine	4.96	3.32	non	non	54.0	28.2	92	83	1.5

¹⁾Mg-rich mica, Predominantly phlogopite

Table 7. Total concentrations (wt.%) of SiO₂, Al_2O_3 , Fe_2O_3 , MgO, CaO, K_2O , and Na_2O , the Si:Al molar ratios of the tailings materials, the concentrations of sulfide sulfur (Aqua regia leachable), and the sum of Aqua regia leachable sulfidic As and chalcophile metal concentrations (Sulfide Me).

Sample ID	Ore	SiO ₂	Al ₂ O ₃	Si/Al	Fe_2O_3	MgO	CaO	K₂O	Na₂O	S	Sulphide
	deposit			molar							Me ¹⁾
	type			ratio							
		wt%	wt%		wt%	wt%	wt%	wt%	wt%	wt%	wt%
		Felsic mi	ning tailing	gs (FMT)							
CERAT2	Gold	57.3	14.3	3.4	5.03	3.14	5.36	4.66	3.91	0.08	0.02
CERAT5	Quartz	89.8	5.16	14.8	0.57	0.11	0.04	1.2	0.11	0.004	0.001
CERAT7	Molybdenum	73.2	11.1	5.6	2.93	4.84	1.95	1.51	3.45	0.02	0.03
		Mining ta	ilings rich	in Mg-Fe-	bearing	minerals	(MgFeMT)				
CERAT1	Apatite-	29.8	7.03	3.6	6.92	16.3	15	5.84	0.47	0.05	0.01
	phlogopite										
		Mining ta	ilings rich	in carbon	ate min	erals ± wo	llastonite	(CMT)			
CERAT10,	Limestone,	44.5	2.92	12.9	1.06	6.42	32.7	0.36	0.74	0.06	0.002
coarse	wollastonite										
CERAT10,	Limestone,	13	1.49	7.4	0.57	1.7	50.6	0.24	0.44	0.03	0.002
fine	wollastonite										

1)The sum of Aqua regia leachable As, Cd, Co, Cu, Mo, Ni, Pb and Zn

Mg- and Fe-bearing minerals (MgFeMT), and mining tailings rich in carbonate minerals (CMT). The last two groups in the present study were each represented by one type of tailings: phlogopiterich tailings grouped in MgFeMT and carbonate and Ca silicate-rich tailings grouped in CMT. The tailings selected here can be considered as inert mining wastes on the basis of very low sulfide sulfur concentrations of <0.1 wt.% (Table 7; see Directive 2006/21/EC). Furthermore, their chalcophile metal and metalloid concentrations were rather low (sum of chalcophile elements \leq 300 mg/kg). More detailed information on the tailings geochemistry results is provided in Electronic Appendix A.

The group name of felsic mining tailings is based on the fact that most of them contained high SiO₂



Figure 1. XRD patterns of the phlogopite sample before (CERA8) and after (CERA8_T) heat tre.atment

concentrations (\geq 65%) and a very low content of silicates rich in Mg and/or Fe (Table 7). According to the petrological classification, the rock is named as acidic rock if the SiO₂ content is \geq 63% (Le Maitre, 1989), which was the case for most of the tailings rich in felsic minerals. In the present study we prefer the name felsic tailing instead of acidic tailing. Adjective acidic rather indicates to acidity released in sulfide oxidation than Si-rich mineral waste and therefore is a misleading term.

The exception was the tailings from gold ore production, which had a somewhat lower SiO_2 concentration, less than 60 wt.%, compared to the others. The quartz-rich tailings contained some K mica, i.e. muscovite, with a content of about 18 wt.%, instead of alkali feldspars.

The tailings sample representing MgFeMT materials had a low SiO_2 concentration of about 30 wt.% (Table 7). The main mineral of the tailings was phlogopite and it contained some carbonates (dolomite, calcite). The coarse fraction of the CMT material predominantly consisted of Ca silicates (>60 wt.%), i.e. wollastonite and diopside, whereas its fine fraction was rich in carbonates (mainly calcite) and had less than 30 wt.% Ca silicates (Table 6). Notably, both tailings materials had minor contents of alkali feldspars and quartz.

3.2 Applicability of MgFeMT materials in geopolymerization

A geopolymer is a synthetic alkali aluminosilicate material produced from the reaction of a solid aluminosilicate, generally kaolin or zeolite, with a highly concentrated alkaline hydroxide and/ or silicate solution (Davidovits, 1994; Xu & van Deventer, 2000). Alkaline dissolution starts to produce soluble Al and Si hydroxides of Al-Si materials, and an undefined gel (Al and Si complex) is then formed. After a short time, the gel hardens into a three-dimensional amorphous and semicrystalline polymer structure with alkali metal compensating for the negative charges caused by Al (Xu & van Deventer, 2002; Davidovits, 2015).

To understand the alkali activation potential of MgFeMT materials, phlogopite mica from apatite production was studied. To increase the dissolution rate of phlogopite, it was formed into a glass. As seen in Figure 1, the untreated phlogopite (CERA8) showed the characteristic diffraction pattern of crystalline phlogopite, whereas after thermal pretreatment, the pattern (of CERAT8_T) was predominantly amorphous with a broad hump from $25^{\circ} 2\theta$ to $45^{\circ} 2\theta$, consistent with predominantly glassy material. The transformation from a



Figure 2. Results of the alkaline dissolution rate test for (a) heated phlogopite (CERA8_T) and (b) metakaolin (M). Results are expressed as the soluble weight percentages of Si and Al based on their amounts in the original material.

crystalline form to an amorphous form is beneficial, as the latter has higher chemical reactivity. According to the XRD pattern, the heated sample (CERAT8_T) contained forsterite (MgSiO₄) as a minute crystalline component.

Both metakaolin and heated phlogopite (CERA8 T) were treated with the alkali solution (NaOH, Fig. 2). Metakaolin rapidly dissolved in the first 24 hours before a plateau in the XRD pattern, whereas phlogopite dissolved slower and did not show a plateau after 100 hours of dissolution. This is not the whole picture, however. After taking into account the finer particle-size distribution of metakaolin and secondary phase precipitation of the heated phlogopite sample, the dissolution rate of the heated phlogopite was close to that of metakaolin (Sreenivasan et al., 2017). In the case of the heated phlogopite, the dissolution process was nearly congruent (the Si:Al ratio of the dissolved species was the same as that in the starting material) until 2 hours, followed by an incongruent regime (Fig. 2). This could be due to aluminium selectively forming more precipitated products compared to silicon. In the case of the heated phlogopite, the Si:Al ratio remained nearly 5 after 24 hours, while the corresponding value in the case of metakaolin was 1 (Fig. 3).

One of the reasons for the above-mentioned deviation is the fact that phlogopite is aluminium deficient when compared to metakaolin (see Table 2). The aluminium content of phlogopite is roughly a quarter of that of metakaolin. It has been reported that a Si:Al ratio close to 2 is desired for geopolymers to have an optimal mechanical strength (Duxson et al., 2005). Hence, an additional aluminum source must be added to the phlogopite-rich material if a durable geopolymer is to be produced from it through geopolymerization. Metakaolin, being an aluminum-rich precursor, is an ideal candidate as a source of aluminum.

All synthesized geopolymers solidified into dense materials (Fig. 4). It was observed that the introduction of thermally treated phlogopite $(CERA8_T)$ to metakaolin improved the compressive strength of the geopolymer (Fig. 5). The silicon solubility of CERA8_T was higher than that of metakaolin, and this could be one of the reasons for the improvement in strength (Sreenivasan et al., 2017). The highest strength (around 12 MPa) was observed in the case of MPG60, a mixture of the thermally treated phlogopite and metakaolin cured at 60 °C. Curing at 80 °C led to a very low compressive strength



Figure 4. Synthesized geopolymers: (a) MG40, (b) MPG40, (c) MPG60, and (d) MPG80 (see Table 3).

(around 1 MPa), which is consistent with the cracks observed in the sample (cf. Figs 4d and 5).

The XRD patterns of metakaolin refer to largely amorphous Al silicate with a broad hump between 15° and 40° (2 θ) centered at 25° (Fig. 6). The only obvious crystalline component detected was anatase (a form of TiO₂ mineral), which is present in the metakaolin as an impurity (see TiO₂ in Table 2). In the case of the geopolymer prepared from metakaolin (MG40), the 25° metakaolin hump was not present (cf. patterns of MK and MG40), which is consistent with a near-complete transformation of metakaolin into a geopolymerization product. The XRD patterns of the geopolymers prepared from the mixtures of the heated phlogopite and metakaolin (MPG40, MPG60, MPG80) were close to that prepared from metakaolin alone (MG40), with an additional amorphous phase at around 10° (2 θ , Fig. 6). It can be concluded that the geopolymers are amorphous in nature, which accounts for the broad hump between 25–45° (2 θ), centered at 32°. These results provide evidence that the pretreated



Figure 5. Compressive strength (MPa) of the synthesized geopolymers (MG, MPG40, MPG60, and MPG80; see Table 3).





MgFeMT material (rich in phlogopite) can be used as an early strength-enhancing additive in metakaolin-based geopolymers. The mode of action and effect on the long-term strength and durability warrant more attention and will be the subjects of further study.

3.3 Applicability of mining tailings to phosphate-bonded ceramics

As with the alkali-activated cements and geopolymers, phosphate bonding offers a route to forming ceramic-like structures in low temperatures. Instead of requiring a highly alkaline solution, phos-

phate formation occurs under acidic conditions when a sufficient amount of soluble mineral matter and a source of phosphate (PO_4^{3-}) are present. The most suitable laboratory-grade raw materials are sparsely soluble divalent oxides, such as MgO, CaO, and ZnO, as well as Al₂O₃ and oxides of iron (FeO, Fe_2O_3 , Fe_3O_4), with some limitations (Wagh, 2013). The good chemical stability and thus low solubility of most naturally occurring silicate minerals, such as the ones characteristic of the tailings in this study, prevents them from being utilized for room-temperature phosphate bonding. Rare examples of reactive silicates include wollastonite (CaSiO₂) and tricalcium silicate (Ca₃SiO₅), the former being especially promising as a raw material for structural applications (Colorado et al., 2015). Phosphate ceramics can be produced from clay minerals as well, and they are in these cases commonly referred to as "phosphoric acid-based geopolymers" due to their structure consisting of alternating tetrahedral $[AlO_4]$, $[SiO_4]$, and [SiO₄] units (Davidovits, 2015). From Al silicates, metakaolin and illite-bearing clays have been successfully used as raw materials for phosphatebased geopolymers (Colorado et al., 2015; Louati et al., 2016). Maslova et al. (2008) used sphene as a raw material for a phosphate geopolymer.

The CMT material from the calcite and wollastonite flotation contained 20-30 wt.% of wollastonite, depending on the grain size, in addition to diopside and calcite (Table 6). Diopside and wollastonite are chain silicates comparable with alkali polyphosphates (see Davidovits, 2015), and it is therefore expected for them to have a high enough reactivity to transform into a phosphate gel following phosphoric acid treatment, and even to subsequently harden into a solid material. However, the surprisingly high reactivity of other calciumbearing minerals present in the CMT material took precedence over any noticeable wollastonite-based phosphate bonding.

Figure 7 presents the XRD spectra for the coarse and fine CMT material (CERAT10) after the two exposure tests described earlier. For the coarse fraction in Figure 7a, some prominent peaks of

calcite and dolomite appeared to visibly diminish, whereas the characteristic peaks for wollastonite remained similar, although not identical, in terms of relative intensity throughout different exposures. The fine-grained fraction of the CMT material responded quite differently to acid treatments compared to its coarse-grained counterpart (Fig. 7b). The characteristic peak intensities of diopside and wollastonite were diminished, while calcite intensities remained very static. Compared to the calcite reactivity observed in the coarse fraction, this was unexpected, since a reduced grain size would commonly translate into an increased reactive surface area and thus higher reactivity overall.

The formation of brushite (CaHPO₄·2H₂O) (see Fig. 7a) confirms that a significant amount of dissolved calcium was available in the post-treatment mixture of coarse CERAT10. This indicates that a calcium-bearing mineral chemically reacts with phosphoric acid during exposure. Figure 8a displays newly formed calcium phosphate flakes in the coarse CERAT10 after drying. The rough texturing on diopside (Fig. 8b) and minor cracking on wollastonite (Fig. 8c) grains support the relative intensity changes observed in XRD analysis of the coarse fraction. The presence of silicon in EDS for calcium phosphate is due to the surrounding smaller grains of primary minerals.

Further solubility testing for coarse CERAT10 was performed in 1.0% and 2.5% H₃PO₄ solutions (see Fig. 9). The focus in this case was not on the newly formed phosphate species, but rather on the clearer identification of minerals that are soluble under these conditions. Calcite showed very high reactivity in both solutions, significantly decreasing in characteristic XRD peak intensity after 1% washing and completely disappearing in the 2.5% solution. Wollastonite intensities remained high in 1% solution and were greatly reduced in a 2.5% wash. The results for diopside were the least conclusive due to the characteristic peaks being severely masked by other minerals in the XRD spectrum, especially in untreated reference tailings.



Figure 7. XRD patterns of the coarse (a) and fine (b) CMT samples (CERAT10) in different stages of H3P04 exposure. Untreated fractions of CERAT10 and a commercial wollastonite, W325 (d50 = $12.5 \mu m$), originating from the same ore source are shown for reference.

Despite showing signs of high reactivity in SEM analysis, a significant amount of diopside appears to have remained after washing in both solutions. While clear conclusions on diopside solubility cannot be drawn from these results, they do not clearly exclude the reactivity of the mineral. Beyond tailings sample CERAT10, no clear results were obtained from the XRD analysis of acid-treated samples. This was most likely due to the masking effect that some minerals such as quartz and several micas can have on XRD results, where the strong characteristic peaks of these minerals can



Figure 8. Calcium phosphate lamellae in CERAT10 (Coarse) after 2.5% acid exposure for 24 h and subsequent liquid evaporation (a). Diopside (b) and wollastonite (c) show surface degradation compared to the as-received state (d) and (e), respectively.



Figure 9. XRD patterns of coarse CERAT 10 after a 60-min wash in 1% and 2.5% H3PO4 solutions.

even obscure some significant intensity changes and new peaks. Automated data processing of single measurements was found to be inaccurate for the purposes of studying these changes in the complex mineralogy.

The XRD results for acid-treated fractions were largely inconclusive and did not give a complete picture of how the tailing fractions behaved when exposed to dilute orthophosphoric acid. Specifically, the CERAT2 sample from the FMT material of the gold mine, which contains a fair percentage (7 wt.%) of calcite, produced a clear component of calcium phosphate after 24 h exposure to 2.5% H₃PO₄ (see Figure 10), despite this not significantly showing in the XRD results. The CERAT2 sample also contained albite, from which, according to Davidovits (2015), Al can be dissolved by phosphoric acid at 750 °C, followed by the formation of AlPO_4 and a poly(sialate-siloxo) system, a potential composite for phosphatebonded ceramics. However, no evidence was found of albite in that sample noticeably reacting with phosphoric acid during the room-temperature exposure tests. This result was consistent with the findings from other exposure tests, where calcite mineral appears to have taken precedence in reactions with dilute orthophosphoric acid, even when another potentially reactive component, which in the case of CERAT10 was wollastonite, was present.

Preliminary tests of the phosphoric acid treatment showed that calcite reacted with the acid, forming Ca phosphate lamellae. However, the results for wollastonite, diopside, and albite were inconclusive and appeared to be more dependent on the specific set of conditions.

3.4 Applicability for reaction sintered ceramics

The mullitization temperature differs considerably depending on the synthesis method and Si:Al ratio used (Klug et al., 1987). The splintery mullite mineral has beneficial properties for use in the ceramics industry, i.e. a high melting point, low thermal conductivity, moderate thermal expansion coefficient, and good chemical resistance. Mullite ceramics have been synthesized, for example, from



Figure 10. Calcium phosphate lamellae formed in tailings CERAT2 after 2.5% H3PO4 exposure for 24 h.



Figure 11. Mixtures SIN01-SIN06 after sintering at 1300 °C for 3 h (see Table 5).



Figure 12. XRD pattern for mine tailings CERAT2 and for SIN01 (CERAT2 + AI) and SIN02 [CERAT2 + AIO(OH)] mixtures after heat treatment at 1300 °C for 3 h.

kaolinite (Sainz et al., 2000), sillimanite (Tripathi & Banerjee, 1999), and andalusite (Sardy et al., 2012).

After sintering, the mixtures (SIN03 and SIN05) of the FMT materials (CERAT5, CERAT7) and Al powder had a greyish color, whereas the tailings mixtures with boehmite had a white color (Fig. 11). The mixtures (SIN01 and SIN02) containing CERAT2 tailings with both Al additions had a reddish color. Furthermore, mixtures containing aluminum and boehmite had differences in shrinkage, as shown in Figure 11.

After the reaction sintering, the tailings sample CERAT2 with the two alumina sources showed quite identical XRD patterns, attributed to corundum as the main crystalline phase (Fig. 12). It appears that muscovite, albite, K-feldspar, and quartz did melt and a new aluminosilicate crystalline phase was formed, in addition to the corundum phase.

Mixtures (SINO4, SINO3) with CERAT5 tailings (from the quartz mine) and Al additions after the reaction sintering resulted in very different phase structures depending on the aluminium source used (Fig. 13). The mixture with aluminum powder (SIN03) resulted in a corundum phase structure together with metallic silicon and metallic aluminum phases (Fig. 13). It appears that both quartz and muscovite melted during the reaction sintering. When using boehmite (SIN04) as the aluminium source, an XRD pattern attributed to quartz and corundum phases and also mullite peaks were visible (Fig. 13). In addition, small



Figure 13. XRD patterns for CERAT5 mine tailing and for SIN03 (CERAT5 + AI) and SIN04 [CERAT5 + AIO(OH)] mixtures after heat treatment at 1300 °C for 3 h.

peaks of cristobalite were seen, which indicates a quartz reaction. These results indicate that only part of the quartz had melted, because quartz peaks were still visible after sintering. On the other hand, muscovite appears to have melted during the reaction sintering, with resulting mullite peaks in the reaction sintered pattern (SIN04).

Similarly to the above patterns, there were clear differences in XRD patterns after reaction sintering between different aluminium sources mixed with CERAT7. The mixture with aluminum powder (SIN05) resulted in a corundum phase together with metallic silicon and aluminum phases (Fig. 14). It appears that muscovite, quartz, and albite phases again melted during the heat treatment and new crystalline phases appeared. After reaction sintering of the mixture with boehmite (SIN06), a mullite and corundum phase structure resulted (Fig. 14). During the heat treatment, quartz, muscovite, and albite melted, resulting in a mullite and corundum phase structure.

These preliminary results indicate that FMT materials are potential raw materials for mullitebased ceramics if an additional aluminium source is used. We detected differences in reactivity between the tailings materials and mixtures of them with two types of aluminium sources. Thus, future research will be needed to fully understand the potential of FMT materials as raw materials in mullite-based ceramics.



Figure 14. XRD patterns for mine tailings CERAT7 and for SIN05 (CERAT7 + AI) and SIN06 [CERAT7 + AIO(OH)] mixtures after heat treatment at 1300 °C for 3 h. The mixture SIN05 shows XRD reflections of an unknown aluminosilicate formed during sintering.

3.5 Key factors defining tailings utilization in ceramics manufacturing

Mining tailings generated from ore deposits in felsic and intermediate rock environments have alkaline aluminosilicates in addition to quartz as major minerals. One could argue that tailings (FMT) from these ore productions are viable in geopolymerization based on their oxide content (see Xu & van Deventer, 2002; Feng et al., 2012). Several researchers have recommended that the Si:Al ratio for a viable geopolymer is <3, the optimal ratio being ≤ 2 (Provis, 2006; Duxson et al., 2007; Xu & van Deventer, 2000). The ratio for the studied

FMT materials varied between 3.2 and 5.6 (except for CERAT5: 14.4), which indicates the need for Al additives (Ahmari & Zhang, 2012). Using NaOH as an alkali activator and albite-bearing tailings as a precursor, the Na:Al ratio can be a critical factor affecting the structure of geopolymer gels (Zhang et al., 2011, see also Feng et al., 2012). Ahmari & Zhang (2012) argued that too high a Na:Al ratio (or too high NaOH:MT) will lead to excess metal cations in the polymeric network and adversely affect the mechanical properties of geopolymers. However, the FMT tailings had not yet been tested in geopolymerization in the present study. Instead, the experiment with mixtures of heated phlogopite and metakaolin gave promising results for the viability of MgFeMT materials in geopolymerization. The introduction of thermally treated Mg silicate to metakaolin improved the compressive strength of the geopolymer.

Phosphate formation, much like geopolymerization, is heavily dependent on a sufficiently high solubility of precursors. In the current state, none of the listed tailing fractions are usable for phosphate bonding at the macroscopic level, i.e. for producing bulk ceramic pieces. Excessive dissolution of metal salts hindered the formation of a three-dimensional network, whereas low solubility did not provide enough ions to form solid reaction products. Nevertheless, three fractions produced promising results in terms of phosphate reactivity: CERAT2 from the gold mine and the two CERAT10 fractions from the limestone-wollastonite mine. The majority of the observations relate to the high reactivity of calcite and the resulting crystalline phosphate phases. However, diopside in coarse CERAT10 also showed signs of dissolution, and not all of the dissolved calcium can therefore be necessarily attributed to calcite in this instance. Additionally, wollastonite was found to have a minor response to the acid exposure, despite the presence of more reactive minerals. Further prioritization of wollastonite as a Ca source would require the removal of calcite and diopside as Ca donors. Options for achieving this are thermal treatments and pre-reacting of excessively reactive components. The complete or partial removal of calcite was shown to be possible by washing the tailings fraction in an excessive amount of dilute phosphoric acid solution for 60 minutes, although this approach also moderately reduced the amount of wollastonite.

Most aluminum silicates are able to form mullite as a reaction product when heated at high temperatures. For natural mullite, the ratio lies between relatively SiO_2 -rich 3:2 mullite to aluminium-rich 2:1 mullite. The FMT materials in sintering ceramic tests had an Al_2O_3 :SiO₂ ratio of under 1:4, which inevitably leads to the need for an additional Al source in order to form mullite. Preliminary mullite reaction sintering experiments showed the potential of FMT materials as raw materials in mullite-based ceramics, but the resulting phase structures depend on the type of additional aluminium source and also the chemical composition and mineralogy of FMT materials. Additional research will be needed to verify their effects.

4. Conclusion

The present study valorized tailings from five Finnish mines to identify their viability for ceramics production. On the basis of their mineralogical and chemical contents, the tailings were grouped into FMT materials rich in quartz and alkali feldspars, MgFeMT materials rich in Mg and Fe-bearing silicates, and CMT materials rich in carbonate minerals and Ca silicates. Experimental work demonstrated that MgFeMT materials with an added Al source (here metakaolin) are viable for geopolymerization. Based on a literature review, FMT materials can be potential source materials for the production of geopolymers, but a high initial Si:Al ratio (in quartz-rich FMT) may lead to partial geopolymerization. Reaction sintering experiments, however, showed their viability for mullite-type ceramics. Experiments with CMT materials yielded promising results in terms of phosphate reactivity, but none of the tailings of the present study were usable for phosphate bonding at the macroscopic level, i.e. for producing bulk ceramic pieces.

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Supplementary data

Electronic Appendix A for this article is available via Bulletin of the Geological Society of Finland web page.

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