



Characterization and thermal analysis of metalworking sludge as a partial substitute for clays in ceramic production

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Abstract

This study evaluates the feasibility of using sludge from the metalworking industry (SMWI) as a partial substitute for clays in producing red ceramics for civil construction. The analysis of the white goods production process predicted the components of SMWI, potentially reducing the need for additional chemical analyses. According to the chemical analyses provided, SMWI is a non-hazardous solid waste, but not inert, due to the presence of aluminum, chlorine, and phenols, by Brazilian standards. The oxide composition of SMWI showed compatibility with the studied clays and data from the literature, suggesting its potential as an additive in ceramics. Rich in CaO and Al₂O₃, SMWI can enhance the mechanical strength of ceramics, although excessive addition may increase water absorption. Loss on ignition tests, thermogravimetry, and SEM-EDS analyses on SMWI and pure and 5% SMWI-added clays revealed the loss of volatile compounds and the formation of thermostable clay minerals. However, its distinct composition, with lower levels of Fe₂O₃ and SiO₂, and the need for adequate homogenization, requires caution to avoid impacts on the final properties of the ceramic products, such as water absorption and mechanical strength. Thus, the use of SMWI as a ceramic additive presents itself as a sustainable and viable alternative, although further studies are necessary to validate its application in compliance with Brazilian technical standards.

Keywords: Sustainable Management; Industrial Sludge; Pollutant Prediction; Waste Valorization; Clay Substitution.

Caracterização e análise térmica de lodo metalmecânico como substituto parcial de argilas na produção cerâmica

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Resumo

Este estudo avalia a viabilidade de utilizar o lodo da indústria metalmeccânica (SMWI) como substituto parcial de argilas na produção de cerâmicas vermelhas para a construção civil. A análise do processo de produção de eletrodomésticos previu os componentes do SMWI, potencialmente reduzindo a necessidade de análises químicas adicionais. Segundo as análises químicas previstas, o SMWI é um resíduo sólido não perigoso, mas não inerte, devido à presença de alumínio, cloro e fenóis, conforme as normas brasileiras. A composição de óxidos do SMWI mostrou compatibilidade com as argilas estudadas e dados da literatura, sugerindo seu potencial como aditivo em cerâmicas. Rico em CaO e Al₂O₃, o SMWI pode aumentar a resistência mecânica das cerâmicas, embora a adição excessiva eleve a absorção de água. Ensaios de perda ao fogo, termogravimetria e MEV-EDS no SMWI e em argilas puras e aditivadas com 5% revelaram a perda de compostos voláteis e a formação de argilominerais termoestáveis. No entanto, sua composição diferenciada, com menores teores de Fe₂O₃ e SiO₂, e a necessidade de uma homogeneização adequada exigem cautela para evitar impactos nas propriedades finais das cerâmicas, como absorção de água e resistência mecânica. Portanto, o uso do SMWI como aditivo cerâmico surge como uma alternativa sustentável e viável, mas estudos complementares são necessários para validar sua aplicação conforme as normas técnicas brasileiras.

Palavras-chave: Gestão Sustentável; Lodo Industrial; Previsão de poluente; Valorização de Resíduo; Substituição de argila.

1 Introduction

The following section presents the relevance of using industrial waste, particularly metallurgical sludge, as an alternative raw material in ceramic production. Based on environmental regulations and the growing need for sustainable practices, this study investigates the potential of incorporating such waste into brick manufacturing raw material as a final destination. Through detailed chemical and thermal analyses, the research aims to assess the feasibility of replacing natural clays with metallurgical sludge, highlighting its environmental and economic benefits while addressing key industrial challenges.

The generation of large volumes of urban and industrial waste is a pervasive challenge, often unavoidable but undesirable. Like the European Union Directive 2008/98/EC (EU, 2008), Brazil's National Solid Waste Policy, Law No. 12,305 of August 2, 2010 (BRASIL, 2010), sets up clear guidelines to inform decision-making processes. This legal framework prioritizes actions in the following order: prevention of waste generation, reduction, reuse, recycling, treatment, or, eventually, environmentally final disposal. Within this context, the incorporation of urban solid waste, such as beached sargassum, into the production of construction materials offers a practical pathway to mitigate various environmental impacts associated with land use (Parente et al., 2024).

In a similar context, the treatment of water for human consumption, sewage, and industrial effluent generates sludge through processes such as coagulation, flocculation, and precipitation (Richter, 2001; Metcalf & Eddy, 2015). The chemical and physical properties of sludge vary depending on the characteristics of the water, industrial inputs, and specific

treatment processes (Ahmad; Ahmad; Alam, 2016). For instance, the metalworking industry (SMWI) produces predominantly inorganic sludge, primarily composed of aluminum oxide, a byproduct of the coagulants used (Vieira; Silva, 2012). According to Brazil's National Solid Waste Policy (BRASIL, 2010), this type of solid waste can potentially be treated to recover the coagulant agent for reuse as a contaminant and heavy metal adsorbent in effluent treatment, as well as in various applications such as construction materials, soil additives in agriculture, and as a secondary raw material for cement and brick manufacturing (Ahmad; Ahmad; Alam, 2016). Coagulation sludges that share comparable properties with clays used in ceramic production can partially replace this primary raw material, conserving natural resources (Tartari et al., 2011; Sutcu et al., 2022). This approach significantly mitigates environmental impacts, including soil erosion, water contamination, disruptions to local flora and fauna, deterioration of air quality, noise pollution, and the loss of landscape value due to clay extraction. It also addresses socio-environmental conflicts (López-Juvinao; Torres-Ustare; Moya-Camacho, 2020) and reduces the need for rehabilitating degraded areas (Turrión et al., 2021). Thus, the valorization of coagulation sludge as a partial substitute for clay in ceramic brick production is a sustainable resource management strategy (Ahmad; Ahmad; Alam, 2016) that aligns with recycling principles (EU, 2008; BRASIL, 2010).

Several studies have demonstrated promising results when incorporating various types of sludge into ceramic bricks, including metalworking sludge (Vieira; Silva, 2012), ceramic sludge (Coletti et al., 2016), tannery sludge (Juel; Mizan; Ahmed, 2017; Hasan; Hashem; Payel, 2022), marble sludge (Munir et al., 2018), papermaking and sugar carbonation sludge (Yaras, 2020), dairy factory sludge (Simón et al., 2021), water treatment plant sludge (Oliveira; Holanda, 2008; Tartari et al., 2011; Benlalla et al., 2015; Sutcu et al., 2022), and urban wastewater effluent sludge (Martínez-García et al., 2012; Zhang et al., 2016; Ukwatta et al., 2015; Ukwatta et al., 2016; Ukwatta; Mohajerani, 2017). Red clays, typically used in brick production, contain iron-rich materials with Fe_2O_3 levels above 3%, carbonates below 10%, and a coarse-grained fraction under 25% (Dondi; Raimondo; Zanelli, 2014). Therefore, prior characterization of both clays and raw materials is essential to find necessary adjustments for incorporation into the ceramic mass during the industrial process (Macedo et al., 2008; Savazzini-Reis; Della-Sagrillo; Valenzuela-Díaz, 2016; Boukili et al., 2021). Additionally, incorporating sludge into bricks can encapsulate pollutants, preventing them from leaching at concentrations exceeding legal limits (Juel; Mizan; Ahmed, 2017).

In this context, the objective of this study was to develop a methodology for predicting the composition of sludge from the white goods metalworking industry (WMI) based on the industrial process, to characterize WMI sludge in terms of pollutants, and to evaluate its potential as a partial substitute for clays used in ceramic brick manufacturing.

2 Materials and methods

2.1 Assessment of pollutants that make up the SMWI of the white goods process

Technical visits were conducted in collaboration with production area professionals to predict the pollutants present in sludge from the metalworking industry (SMWI). This sludge is generated during the physical-chemical treatment of industrial wastewater in the metalworking process of a white goods company in Curitiba.

2.2 Obtaining SMWI and red ceramic production clays

The SMWI samples were provided by a white goods industry in Curitiba. Samples were collected at various stages of the process to capture the variability of SMWI over time.

The clays used in this study, named as A0 and B0, were generously donated by ceramic brick manufacturers in Curitiba (Clay A0) and São José dos Pinhais (Clay B0), both in Paraná, Brazil. The modified clays, labeled A5 and B5, were produced by adding 5% dry SMWI (by mass) to the original clays.

2.3 Analysis of SMWI and donated clays

The SMWI, along with the clays provided in their natural state (A0 and B0) and those changed with 5% (by mass, on a dry basis) SMWI (A5 and B5), underwent a series of analyses.

2.3.1 Assessment of the Dangerousness and Inertibility of SMWI

The toxicity of SMWI was evaluated following the methodologies outlined in SW 846 of the United States Environmental Protection Agency (USEPA) Test Methods for Evaluating Solid Waste: Physical/Chemical Methods Compendium - Report Number 846 (USEPA, 1986). Various parameters were assessed using specific methods, including Method 245.7 (1986), Method 3510C (1996), Method 8260C (2006), Method 9010C (2004), Method 9034 (1996), Method 9045D (2004), and Method 9213 (1996). The SMWI was then classified according to its hazardousness and inertness in its natural state, following Brazilian standard NBR 10.004 (ABNT, 2004a), and its leaching extract was evaluated according to NBR 10.005 (ABNT, 2004b) and NBR 10.006 (ABNT, 2004c). A detailed chemical analysis of the solubilized material was performed, focusing on inorganic parameters such as aluminum, arsenic, barium, cadmium, chromium, copper, iron, lead, manganese, mercury, selenium, silver, sodium, zinc, chloride, cyanide, fluoride, nitrate, and sulfate. Additionally, pesticides, including aldrin + dieldrin, chlordane, DDT and its isomers, 2,4-D, endrin, heptachlor and its epoxides, lindane, methoxychlor, pentachlorophenol, toxaphene, 2,4,5-T, and 2,4,5-TP, were identified. The analysis also detected other hazardous organic compounds such as benzene, benzo(a)pyrene, vinyl chloride, chlorobenzene, chloroform, total cresol (m+p), o-cresol, 1,4-dichlorobenzene, 1,2-dichloroethane, 1,1-dichloroethylene, 2,4-dinitrotoluene, hexachlorobenzene, hexachlorobutadiene, hexachloroethane, methyl ethyl ketone, nitrobenzene, pyridine, carbon tetrachloride, tetrachloroethylene, trichloroethylene, 2,4,5-trichlorophenol, and 2,4,6-trichloropheno.

2.3.2 Determination of Loss on Ignition and Thermostability of SMWI and Clays

The loss on ignition (LoI) of the dried (at 105°C to constant mass) samples was found gravimetrically by calcination in a muffle furnace at 1000°C for 2 hours (Parente et al., 2024). Additionally, the mass loss evolution was assessed through thermogravimetric analysis (TGA) using approximately 15 mg of sample. The samples were heated at a rate of 10°C/min from 30°C to 995°C in a nitrogen atmosphere (20 mL/min) using a TGA 4000 System by Perkin Elmer (Bernal et al., 2017).

2.3.3 Determination of SMWI Oxides and Clays

The elements in the SMWI and the clays donated in natura (A0 and B0) were analyzed after being dried in an oven at 105°C for 24 hours. A 7 g part of each dried sample was mixed with a resinous material and pressed for analysis by wavelength-dispersive X-ray fluorescence (WD-XRF) using a PANalytical AXIOS spectrometer equipped with a rhodium X-ray tube (Gazulla Barreda et al., 2016).

2.3.4 Scanning Electron Microscopy and Energy Dispersive Spectrometry Analysis of SMWI and Clays

The residues of the sintered samples from the TGA analysis were examined using scanning electron microscopy (SEM) on a TESCAN VEGA3 LMU microscope at magnifications up to 200kX. Microanalysis of the samples was performed through Energy Dispersive X-ray Spectroscopy (EDS) using an Oxford system equipped with an 80 mm² SDD-type detector. The analysis was conducted on selected fields with the help of AZtech (Advanced) software (Nunes et al., 2023).

3 Results and discussion

This section presents a comprehensive evaluation of the potential use of metalworking sludge (SMWI) as a substitute for clay in ceramic production, offering an alternative to more costly disposal methods such as industrial landfilling. The analysis begins with predicting the potential pollutants present in SMWI, based on the industrial processes and chemicals used in home appliance manufacturing. SMWI was chemically characterized for classification as "solid waste" under Brazilian regulatory frameworks, determining its suitability for reuse or appropriate disposal in line with Brazil's National Solid Waste Policy.

In addition, the chemical characterization of SMWI and two donated clays, commonly conducted in the ceramic industry, enabled comparisons of SMWI with other industrial and wastewater treatment sludges previously proposed as clay additives. The donated clays were also assessed with other reported clay materials.

The study further investigates the feasibility of incorporating up to 5% SMWI into the clays by evaluating the thermostability and microstructural behavior of pure clays and those mixed with SMWI, focusing on their thermal properties and stability. Lastly, the microstructural and compositional analysis of SMWI and clays provides detailed insights into the changes that occur after adding SMWI, supporting the proposed valorization of SMWI to reduce the demand for clay as a raw material in the production of ceramic parts for civil construction.

3.1 SMWI pollutant potentials from the white goods process

The production process for painted metal parts in the white goods industry involves multiple unit operations (depicted in gray in Figure 1), which use various chemical products (shown in green) and generate industrial effluent. After treatment, this effluent produces contaminated oil, treated wastewater, and sludge from the metalworking industry (SMWI, marked in orange). The used oil (depicted in pink) is sent for treatment, while the treated wastewater (in dark blue) meets acceptable discharge standards, such as keeping a pH between 5.0 and 9.0, by Conama Resolution No. 430 (BRASIL, 2011).

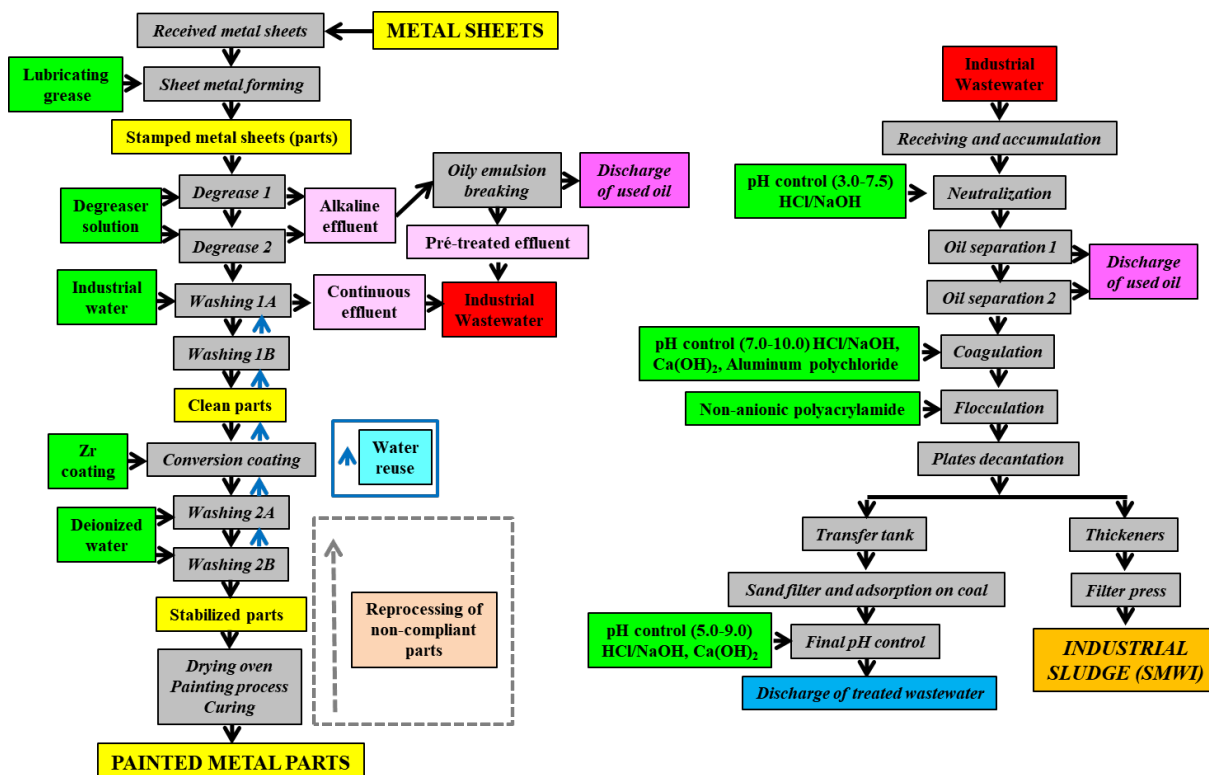


Figure 1: Block diagram of the metal sheet production process and the treatment of Industrial Wastewater (red) that generates sludge (orange) from the metal-mechanical industry (SMWI).

During the production process, metal sheets are initially coated with protective oils and lubricating grease during sheet metal forming. The stamped metal sheets are degreased through an alkaline washing process (Figure 1) using a solution with potassium hydroxide, sodium nitrite, potassium salts, and fatty alcohol (Costa et al., 2012; Costa; Agnoli; Ferreira, 2015). The alkaline effluent generated is pretreated to break emulsions and remove lipid components, which are then sent for specific disposal (e.g., co-processing) and later treated in the industrial wastewater treatment plant (IWT).

Following this, the cleaned metal parts undergo treatment with nanoceramic technology to deposit zirconium layers, enhancing their corrosion resistance (Costa et al., 2012; Costa; Agnoli; Ferreira, 2015; Assemani et al., 2016). These metal parts are washed with deionized water before further operations, without generating more effluent from the process that produces painted metal parts. The alkaline effluent (in light pink, Figure 1) and reused water having dirt, referred to as "continuous effluent" (also in light pink), are combined and sent to the IWT plant (marked in red).

The industrial effluent is then subjected to physical-chemical treatment, which includes pH adjustment with sodium hydroxide or hydrochloric acid for oil separation, coagulation using Ca(OH)_2 and aluminum polychloride, and flocculation with anionic polyacrylamide (in green, Figure 1). The solid fraction from this treatment process leads to the formation of SMWI. A critical analysis of this process predicts that SMWI has certain potential components (Table 1), which will be discussed in further detail later in this study.

Table 1: Contaminants predicted in SMWI according to process analysis.

Process materials	Source	Contaminant
Metal plates	Metal plate components	Fe, Cr, Ni, Zn
Defective painted plates (Reprocessing)	Paint components	Pigments, organic compounds
Alkaline effluents (Degreasing stages)	Alkaline treatment	Oil and greases
Continuous effluents (Washing stages)	Continuous treatment	Zr, F, P, Na, CN, phenols
Aluminum polychloride (APC)	Coagulating agent	Al, Cl
Anionic polyacrylamide	Flocculating agent	Organic compounds
Calcium hydroxide (Lime)	Pre-alkalizing agent	Ca, Si
Sodium hydroxide (Soda)	pH adjustment	Na
Hydrochloric acid	pH adjustment	Cl

3.2 Chemical analysis of SMWI for classification as solid waste

White goods production process analysis enabled the prediction of the components present in SMWI (Table 1), potentially reducing the need for extensive chemical analyses for its characterization. According to the Brazilian standard NBR 10.004 (ABNT, 2004a), waste is hazardous if it shows flammability, corrosivity, reactivity, toxicity, and/or pathogenicity. Non-hazardous waste, on the other hand, is further classified as inert or non-inert based on the analysis of its solubilized extract (ABNT, 2004a, 2004b, 2004c), which directly affects its disposal options (Sisinno, 2003).

In the case of SMWI, it does not display flammability properties, as the oils are removed during pretreatment. Additionally, the chemicals used in the IWT process, such as hydrochloric acid, polyaluminum chloride, anionic polyacrylamide, calcium hydroxide, and sodium hydroxide, do not have flammability characteristics. SMWI is also not considered corrosive, as its pH stays above 2 and below 12.5 (ABNT, 2004a). It is classified as non-reactive due to its low concentrations of cyanides (<250 mg/kg) and the absence of sulfides (<500 mg/kg) (Table 2). Moreover, SMWI is non-pathogenic, derived solely from the physical-chemical treatment of industrial effluents from metalworking processes, unlike sludge produced by biological treatment in sewage plants (Onofre; Abatti; Tessaro, 2015).

Table 2: Characterization of SMWI *in natura* as set up by Brazilian legal instrument

Classification	Parameter	Maximum limit NBR 10.004 (ABNT, 2004)	Content
"Massa bruta" or <i>in natura</i>	pH	2.0 to 12.5	8.53
	Sulfide (H ₂ S)	500 mg/kg	<4.1 mg/kg
	Cyanide (HCN)	250 mg/kg	0.5 mg/kg
	Moisture	% p/p	75.8% w/w

The mechanical dewatering of SMWI using a filter press reduced its moisture content to 75.8%, which could be further minimized with more efficient equipment or supplementary techniques (Metcalf & Eddy, 2015). This moisture reduction decreases transportation costs and makes it more possible to incorporate SMWI directly into clays for ceramic manufacturing. Toxicity was evaluated through comprehensive chemical analysis using leaching and solubilization tests. In the solubilized fraction, inorganic compounds, pesticides, and other hazardous organic substances were absent, except aluminum, barium, chloride, and total phenols. As a result, SMWI was classified as 'non-inert' (ABNT, 2004a) due to elevated

levels of aluminum, chloride, and total phenols in the solubilized material (Table 3), which exceeded the legal limits. Although barium and cresol were detected in the leached fraction, their concentrations remained below the thresholds established by the NBR 10.004 standard (ABNT, 2004a).

Table 3: Components detected in the analysis of leached and solubilized extracts from SMWI.

Classification	Parameter	Maximum limit (mg/L) NBR 10.004 (ABNT, 2004)	Content (mg/L)
LEEACH			
Inorganic	Barium	70.0	0.424
Organic	Total cresol (m+p)	200.0	0.000472
SOLUBILIZED			
Inorganic	Chloride	250.0	402*
	Fluoride	1.5	1.21
	Sodium	200.0	96.2
	Zinc	5.0	0.279
	Aluminum	0.2	0.219*
	Barium	0.7	0.132
	Copper	2.0	0.0200
	Manganese	0.1	0.0110
Organic	Total phenols	0.01	0.21*

Note.: * = it exceeded the limits set by legal standards

In a comparative study of sludge from a similar Brazilian industry, only aluminum (4.45 mg/L solubilized) was found above the legal reference values (Vieira; Silva, 2012), showing potential differences in production and effluent treatment processes. This underscores the importance of individualized analysis of each production process, as the presence or absence of contaminants cannot be generalized.

Specifically, the origin of these pollutants was traced to several sources: fluoride originates from hexafluorozirconate acid used in surface pretreatment processes (Costa; Agnoli; Ferreira, 2015); sodium is introduced via sodium hydroxide used for pH adjustment in IWT; zinc results from the leaching of galvanized metal parts during degreasing with sodium hydroxide; barium, found in the leachate, is derived from pigments in paints used on reprocessed plates (ATSDR, 2016). Further, aluminum and chloride are by-products of polyaluminum chloride, the coagulant used in effluent treatment (Richter, 2001; Martínez-García et al., 2012; Vieira; Silva, 2012, 2012). Phenolic compounds, which are fungicides and bactericides, are traced back to chemical additives applied during metal sheet treatment and painting processes (ATSDR, 2016), with cresol residues (1-hydroxy-4-methylbenzene) originating from preservatives or oils removed from the sheets.

Most components of SMWI can be associated to the materials used in the process (Table 1), except for silica (SiO₂), which is a contaminant from lime. Based on these findings, SMWI is classified as a "Non-Hazardous Waste Class II A – Non-Inert" (ABNT, 2004a). These results confirm the efficiency of process analysis as a method to reduce the need for extensive chemical testing, emphasizing the importance of thoroughly understanding all unit operations and chemical components involved.

Historically, SMWI has been disposed of in industrial landfills, and more recently, has been used in cement co-processing and as a binding agent in civil construction, with the latter options offering lower costs. Industrial landfill disposal is particularly costly and environmentally detrimental, making it a less desirable choice (Sisinno, 2003). Additionally,

energy recovery from SMWI is limited by chlorine (Table 3), as outlined by the parameters in CONAMA Resolution No. 499 (BRASIL, 2020).

Based on Brazil's waste disposal hierarchy (BRASIL, 2010), the recovery of coagulants from sludge (Metcalf & Eddy, 2015; Ahmad; Ahmad; Alam, 2016) was considered economically unfeasible due to the complexity of the required operations. Therefore, integrating sludge into raw materials for ceramic production (Vieira; Silva, 2012; Tartari et al., 2011; Sutcu et al., 2022; Coletti et al., 2016; Juel; Mizan; Ahmed, 2017; Hasan; Hashem; Payel, 2022; Munir et al., 2018; Simón et al., 2021; Benlalla et al., 2015; Oliveira; Holanda, 2008; Martínez-García et al., 2012; Zhang et al., 2016; Ukwatta et al., 2015; Ukwatta et al., 2016; Ukwatta; Mohajerani, 2017) emerges as a viable alternative, provided it does not compromise the quality of the construction products. This approach not only renders SMWI inert but also reduces the need for primary raw materials, thereby offering significant environmental and human health benefits associated with their extraction and processing (Tartari et al., 2011; Sutcu et al., 2022).

3.3 Chemical analyses of SMWI and donated clays

3.3.1. Moisture determination of SMWI in natura and donated clays

The moisture content of SMWI (75.8%) was more than double that of the donated clays (A0 = 29.0% and B0 = 24.0%). This is a crucial factor in the preparation of the ceramic mass before the molding process, whether through extrusion or dry pressing (Dondi; Raimondo; Zanelli, 2014). The high moisture content of SMWI also raises concerns about transportation planning, as the excess water increases the need for more vehicles, fuel, personnel, and associated costs.

3.3.2. Determination of loss on ignition of SMWI and donated clays

"Loss on ignition" (LoI) refers to the weight loss of a material when subjected to elevated temperatures, used to find the content of volatile substances such as crystalline water, organic matter, carbonates, and other compounds that decompose or evaporate at elevated temperatures. For instance, the dehydroxylation of kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) occurs between 400°C and 650°C (Ptáček et al., 2014). The LoI of the unadditivated donated clays (A0 = 10.28% and B0 = 11.37%) was consistent with the average reported for other clays (avg. = 10.63%, standard deviation or DP = 3.76%, and range or R = 14.31%). However, this value was only about 25% of the LoI for the dry SMWI (39.53%), where the LoI can be primarily attributed to organic matter, carbonates, and other materials that are driven off from the sample (Teixeira et al., 2011; Martínez-García et al., 2012; Zhang et al., 2016; Yara, 2020).

3.3.3 Determination of oxides in donated clays

The composition of clays used in commercial ceramics production is primarily composed of SiO_2 , Al_2O_3 , Fe_2O_3 , and CaO (Figure 2), which together account for an average of 90.38% (with a DP of 4.70% and an R of 15.04%) of the total oxide content. This composition can vary widely depending on the clay's extraction area (Macedo et al., 2008) and the specific clay minerals present (Dondi; Raimondo; Zanelli, 2014). SiO_2 and Al_2O_3 are the predominant oxides in these clays, essential for the formation of common clay minerals like kaolinite, illite, montmorillonite, and chlorite, which often contain significant amounts of SiO_2 and Al_2O_3 within their crystalline structures (Savazzini-Reis; Della-Sagrillo; Valenzuela-Díaz, 2016).



Figure 2: Main oxides in clays.

Note.: C1 (Yaras, 2020), B0 (clay donated from São José dos Pinhais), C2 (Hasan; Hashem; Payel, 2022), C3 (Ukwatta; Mohajerani, 2017), C4a, C4b e C4c (Boukili et al., 2021), C5 (Juel; Mizan; Ahmed, 2017), C6 (Martínez-García et al., 2012), A0 (clay donated from Curitiba), C7a e C7b (Benlalla et al., 2015), C8 (Munir et al., 2018), C9 (Oliveira; Holanda, 2008), C10 (Coletti et al., 2016), C11a e C11b (Tartari et al., 2011); C12 (Simón et al., 2021).

The analysis of donated clays (A0 and B0) alongside reported clays show a lack of linear correlation between the major oxides (SiO_2 , Al_2O_3 , Fe_2O_3 , and CaO), which highlights the natural variability in clay composition. SiO_2 content typically exceeds 45%, as seen in both donated clays ($\text{A0} = 62.19\%$, $\text{B0} = 66.12\%$) and most of the reported clays ($\text{avg.} = 56.63\%$, $\text{SD} = 12.94$, $R = 56.63\%$), although there are exceptions, such as C12, with only 18.10% SiO_2 (Figure 2). Al_2O_3 is the second most abundant component, confirmed in the donated clays ($\text{A0} = 26.53\%$, $\text{B0} = 25.05\%$) and most reported samples ($\text{avg.} = 16.82\%$, $\text{SD} = 7.55\%$, $R = 23.39\%$), with some anomalies like C11b and C12.

Fe_2O_3 content, while not always significant, is typically above 3% in clays used for red ceramics (Dondi; Raimondo; Zanelli, 2014), and this trend is reflected in the donated clays ($\text{A0} = 7.04\%$, $\text{B0} = 3.72\%$) and most reports ($\text{avg.} = 11.43\%$, $\text{SD} = 12.18\%$, $R = 50.01\%$), although with outliers such as C11b (31.76%) and C12 (54.30%). The CaO content is typically low, as seen in the donated clays ($\text{A0} = 0.22\%$, $\text{B0} = 0.45\%$) and in certain samples such as C4c, C3, C9, C11a, and C7b. Other oxides are 4.03% of A0 and 4.66% of B0, with broader variability in their content across different samples ($\text{avg.} = 17.92\%$, $\text{SD} = 2.88\%$, $R = 15.04\%$).

The wide variation in clay oxides used in red ceramics production (Macedo et al., 2008; Dondi; Raimondo; Zanelli, 2014) presents a significant opportunity for incorporating

various solid wastes, including SMWI (Sludge from Metalworking Industry). The clays A0 and B0, which are rich in specific oxides, could potentially incorporate high SMWI content, making them an environmentally desirable destination for this waste.

However, it is essential to consider the functional roles of these oxides in the resulting ceramics. For instance: a) SiO_2 : Reduces plasticity and linear shrinkage while increasing ceramic porosity. b) Al_2O_3 : Enhances mechanical strength (Muñoz Velasco et al., 2014). c) Fe_2O_3 : In concentrations above 3-4%, it generates red ceramics upon firing (Ukwatta; Mohajerani, 2017; Savazzini-Reis; Della-Sagrillo; Valenzuela-Diaz, 2016; Rodrigues; Della-Sagrillo; Reis, 2020). If Fe_2O_3 is below 1-2%, it results in white ceramics (Dondi; Raimondo; Zanelli, 2014).

The clays' composition also includes other elements (e.g., K_2O , TiO_2 , MgO , Na_2O , P_2O_5 , SO_3 , ZrO_2 , BaO , and MnO in A0) that contribute to the desired properties of ceramics, such as high mechanical strength (Dondi; Raimondo; Zanelli, 2014; Savazzini-Reis; Della-Sagrillo; Valenzuela-Diaz, 2016).

Wavelength-dispersive X-ray fluorescence (WD-XRF) spectrometry allows for precise and accurate quantification of both major and trace elements, such as Ba, Ce, Co, Cr, Cu, Fe, La, Mn, Ni, Pb, Rb, S, Sr, Ta, Th, U, V, Y, Zn, and Zr (Gazulla Barreda et al., 2016). This analysis is critical in deciding the suitability of the clays for ceramic production, especially when incorporating SMWI, as it ensures that the final product keeps the desired mechanical and aesthetic properties. In conclusion, the incorporation of SMWI into clays A0 and B0 is promising, but careful consideration of oxide content (Table 4) and its effects on the final ceramic properties is crucial for achieving best results.

Table 4: Chemical composition of SMWI and clays by WD-XRF

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	TiO_2	MgO	Na_2O	P_2O_5	ZnO	Cl	SO_3	SrO
SMWI	7.28	25.81	0.66	43.02	3.81	0.17	2.48	1.82	6.62	4.47	3.15	0.33	0.17
A0	62.19	26.53	7.02	0.22	1.23	1.56	0.56	0.11	0.11	ND	ND	0.11	ND
B0	66.12	25.05	3.72	0.45	1.58	1.69	0.56	0.23	0.11	ND	ND	0.11	ND

Note.: ZrO_2 (0.11%), BaO (0.11%) and MnO (0.11%) were found in A0. ZrO_2 (0.11%) and BaO (0.11%) were found in B0. ND = Not Detected.

3.3.4 Determination of SMWI oxides and association with the source of the industrial process

The analysis of SMWI (Sludge from the Metalworking Industry) revealed that its composition is primarily influenced by the chemicals used during effluent treatment and surface pretreatment of metal parts. Specifically, the major part, CaO (43.02%), originates from the use of $\text{Ca}(\text{OH})_2$ as a coagulation adjuvant in the industrial effluent treatment process (Figure 1, Table 1). The high content of Al_2O_3 (25.81%) is attributed to the use of polyaluminum chloride as a coagulating agent, which also contributes to the presence of Cl (3.15%), as Cl can also be traced back to the use of hydrochloric acid for pH control.

Na_2O (1.82%) is due to the use of sodium hydroxide in pH adjustment. It is important to note that part of the sodium chloride and other thermolabile compounds might volatilize during the loss on ignition (LoI), alongside the decomposition of precipitated salts or the dehydroxylation of crystal structures (Savazzini-Reis; Della-Sagrillo; Valenzuela-Diaz, 2016; Rodrigues; Della-Sagrillo; Reis, 2020). ZnO (4.47%) and Fe_2O_3 (0.66%) originated from the washing of metal parts that undergo leaching during surface pretreatment. Other oxides present in SMWI, such as SiO_2 (7.28%), P_2O_5 (6.62%), K_2O (3.81%), MgO (2.48%), and TiO_2

(0.17%), could originate from various stages of the surface pretreatment process, additives in the degreasing solutions, metal surface treatments, or even from contaminants introduced during these processes.

In summary, the composition of SMWI directly reflects the chemicals used in the metalworking process and effluent treatment, with major oxides like CaO and Al₂O₃ contributing playing crucial roles due to their respective uses in coagulation and pH control. The presence of other oxides underscores the complexity of the sludge composition and its potential impact on later processing or disposal options.

3.4 Comparison between the composition of SMWI and other sludges

Due to the acceptable variation in the oxide composition of clays used in the production of red ceramics (Figure 2), various sludges (Figure 3) from different sources—including sewage treatment plant (2 S-STP, 3 S-STP, 4 S-STP, and 5 S-STP), water treatment plant (6 S-WTP, 7 S- WTP, 8 S- WTP, and 9 S- WTP), and several industrial processes such as ceramics (1 S-CER), paper milling (10 S-PAP), tanning (11 S-TAN and 15 S-TAN), dairy processing (12 S-DAI), marble processing (13 S-MAR), carbonation (14 S-CO₂), and metalworking (16 S-MMI), which is the focus of this study (SMWI)—can be considered potential raw materials for ceramic production. These sludges have between 56.55% and 99.39% of a mixture of SiO₂, Al₂O₃, Fe₂O₃, and CaO. This finding also suggests other, less obvious opportunities, such as the disposal of sargassum stranded on beaches, which is organic. Although life cycle analysis has shown that the sintering of algae into ash may not be incredibly helpful, it presents a workable option for addressing beach maintenance challenges, offering a potentially definitive solution with social, economic, and environmental benefits (Parente et al., 2024).

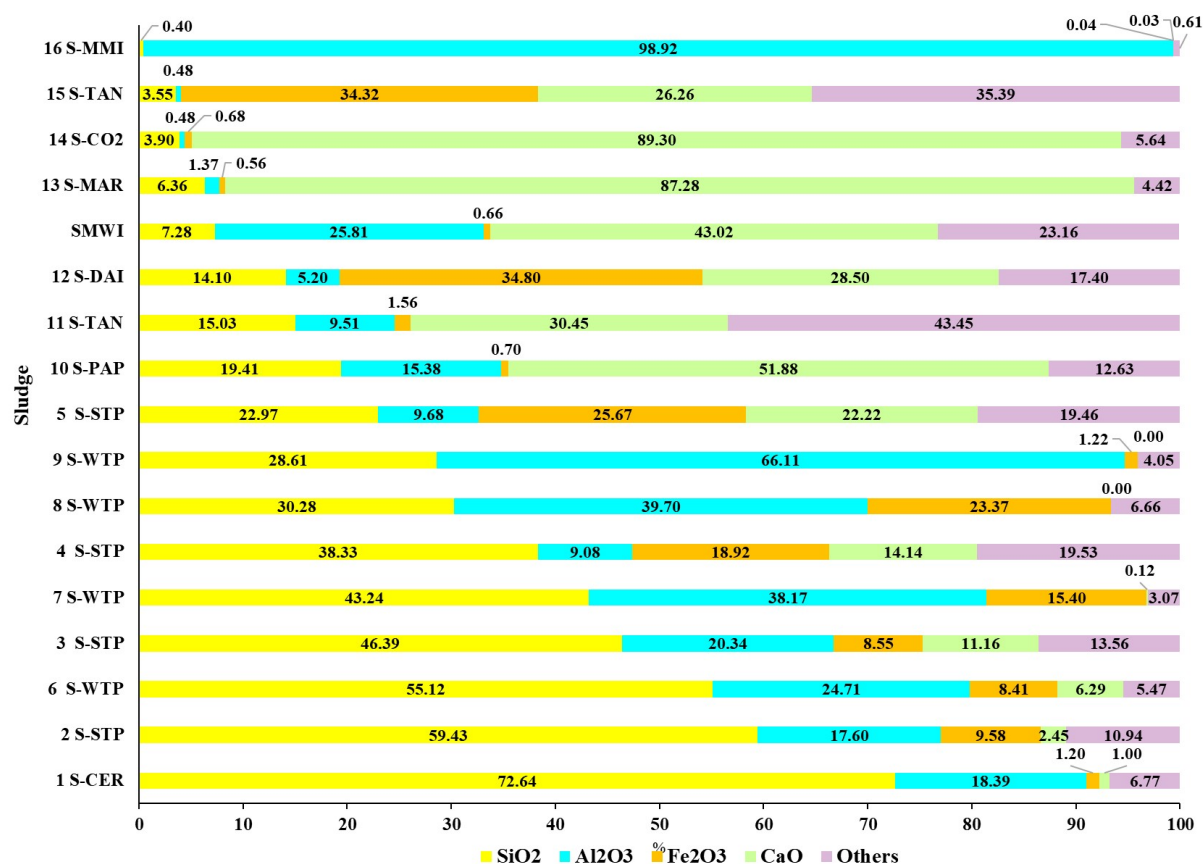


Figure 3: Main oxides in sludge

Note.: 1 S-Cer= Ceramic (Coletti et al., 2016); 2 S-STP= Sewage Treatment Plant (Ukwatta et al. 2016); 6 S-WTP= Water Treatment Plant (Sutcu et al., 2022); 3 S-STP (Martínez-García et al., 2012); 7 S-WTP (Oliveira; Holanda, 2008); 4 S-STP (Ukwatta; Mohajerani, 2017); 8 S-WTP (Tartari et al., 2011); 9 S-WTP (Benlalla et al., 2015); 5 S-STP (Zhang et al., 2016); 10 S-PAP= Paper milling (Yaras, 2020); 11 S-TAN= Tannery (Hasan; Hashem; Payel, 2022); 12 S-DAI= Dairy (Simón et al., 2021); SMWI; 13 S-MAR= Marble (Munir et al., 2018); 14 S-CO2= Carbonation (Yaras, 2020); 15 S-TAN= Tannery (Juel; Mizan; Ahmed, 2017); 16 S-MMI= Metalworking (Vieira; Silva, 2012)

Silicon dioxide (SiO_2) is a desirable part in clays used for ceramic production (Savazzini-Reis; Della-Sagrillo; Valenzuela-Díaz, 2016). Consequently, the sludges analyzed in this study were coded according to their SiO_2 content in decreasing order, except for those from sewage treatment plant (STP) and water treatment plant (WTP). The sludge from the ceramic industry (1 S-CER) showed the highest SiO_2 content at 72.64%, which is consistent with its industrial origin. SiO_2 levels in STP and WTP sludges ranged from 59.43% to 22.97% and 55.12% to 28.61%, respectively, aligning with the presence of sand residues and contaminants from coagulation reagents used in water treatment plant (Richter, 2001; Metcalf & Eddy, 2015). Despite the wide variability in SiO_2 content across industrial sludges (0.40%-72.65%), their incorporation into ceramic production is still possible, albeit with limited addition.

The highest SiO_2 content was seen in ceramic industry sludge (1 S-CER), followed by STP sludge and WTP sludge. In STP, SiO_2 primarily originates from sand particles, while in WTP, it is derived from contaminated CaO used during coagulation (Richter, 2001; Metcalf & Eddy, 2015). Industrial sludges generally contain lower SiO_2 levels (0.40%-19.41%),

reflecting the raw materials and sewage treatment processes employed. The SMWI (sludge from metalworking industry) presents intermediate SiO_2 levels (7.28%), which are significantly lower compared to the lowest SiO_2 content in clay (18.10% in C12), making direct use of SMWI as a raw material for ceramic production unfeasible. Al_2O_3 content varied widely from 0.48% (14 S-CO2 and 15 S-TAN) to 98.92% (16 S-MMI), with combined SiO_2 and Al_2O_3 contents ranging from 4.03% to 99.32%. These variations need cautious addition to ensure the formation of minerals that contribute desirable mechanical properties to the ceramics (Macedo et al., 2008; Dondi; Raimondo; Zanelli, 2014).

The Fe_2O_3 content was notably higher in sludges from dairy (12 S-DAI), tanning (11 S-TAN), and certain STP and WTP treatments, suggesting the possible use of iron ions as a coagulation agent (Richter, 2001; Metcalf & Eddy, 2015). These sludges could serve as additives in red ceramics, while others could be used in white ceramics (Dondi, Raimondo, Zanelli, 2014). SMWI, with a higher Al_2O_3 content (25.81%) and lower Fe_2O_3 content (0.66%), appears to be a superior additive compared to most other sludges, except for the sludge from another metalworking industry (16 S-MMI), which has 98.92% Al_2O_3 and 0.04% Fe_2O_3 . However, it is important to note that sludge from the metalworking industry is not universally the best additive, as this depends on the specific effluent treatment processes applied.

Calcium oxide (CaO) is present in over 25% of industrial sludges (14 S-CO2, 13 S-MAR, 10 S-PAP, SMWI, 11 S-TAN, 12 S-DAI, 15 S-TAN), except for 1 S-CER and 16 S-MMI, which can be attributed to the raw material matrix and effluent treatment principles. The metalworking sludge from another Brazilian industry (16 S-MMI) was composed of Al_2O_3 (98.92%), with small amounts of other oxides such as SO_3 , SiO_2 , K_2O , Fe_2O_3 , CaO , Cr_2O_3 , ZnO , MnO , and CuO (Vieira, Silva, 2012). The differences between this sludge and SMWI can be attributed to variations in the treatment processes and the operational diversity of industrial effluent treatment plants.

In conclusion, the similar Al_2O_3 content between SMWI and clays (A0 and B0) suggests that their mixing is possible (Table 4). However, this is not the case for SiO_2 . Nonetheless, the addition of SMWI can be improved based on the composition of other clays like C18b ($\text{SiO}_2=46.10\%$, $\text{Al}_2\text{O}_3=30.39\%$) and C8b ($\text{SiO}_2=43.13\%$, $\text{Al}_2\text{O}_3=28.43\%$). The high CaO content (43.0%) in SMWI can compensate for its low levels in A0 (0.22%) and B0 (0.45%), potentially enhancing the mechanical strength of the final ceramic product by reacting with SiO_2 in the clay. However, the addition must be carefully controlled to prevent the formation of free CaO in ceramics used in civil construction, which could lead to undesirable water absorption (Muñoz Velasco et al., 2014; Rodrigues; Della Sagrillo; Reis, 2020). The presence of other oxides (23.16%), such as K_2O (3.81%), MgO (2.48%), and Na_2O (1.82%), contributes to the formation of minerals like illite, montmorillonite, and chlorite, which enhance the mechanical strength of the ceramics (Savazzini-Reis; Della-Sagrillo; Valenzuela-Diaz, 2016).

Therefore, SMWI can be considered a desirable additive for both red and white ceramic industries (Muñoz Velasco et al., 2014; Rodrigues; Della Sagrillo; Reis, 2020), ending the costs associated with its disposal in industrial landfills or stabilization treatment. The valorization of this waste reduces the overall production costs for construction materials (Sutcu et al., 2022) and has a socially beneficial effect by minimizing competition for land use (Parente et al., 2024). Further studies are needed to decide the technical feasibility of using SMWI as an additive in red ceramic production.

3.5 Thermostability of SMWI, pure clays and with 5% of their addition

The mass evolution during the sintering process, as predicted by thermogravimetric analysis (TGA) during brick firing, shows similar profiles for the donated clays (A0 and B0) and the clays with 5% additive (by mass, A5 and B5), with some variation in the peak temperatures for specific events (Figure 4a and 4b). The mass loss (WL) of the untreated SMWI was 83.17% between 30°C and 995°C. Specifically, for SMWI, the mass loss (WL_{SMWI}) was 40.96% up to 105°C and 71.40% up to 155°C (Figure 4c), with peaks at 93°C and 103°C, which can be attributed to the elimination of free and adsorbed or occluded water (Savazzini-Reis; Della-Sagrillo; Valenzuela-Diaz, 2016; Boukili et al., 2021). The WL_{SMWI} up to 600°C was 6.23% (Table 5), consistent with the decomposition of organic matter (Yara, 2020; Zhang et al., 2016), hydroxides (Teixeira et al., 2011), and the elimination of low-volatility compounds (Martínez-García et al., 2012). The lower WL_{SMWI} between 155°C and 600°C compared to the clays aligns with the lower organic compound content in industrial waste and the presence of high levels of Al_2O_3 and CaO , which contribute to the formation of thermostable clay minerals (Savazzini-Reis; Della-Sagrillo; Valenzuela-Diaz, 2016).

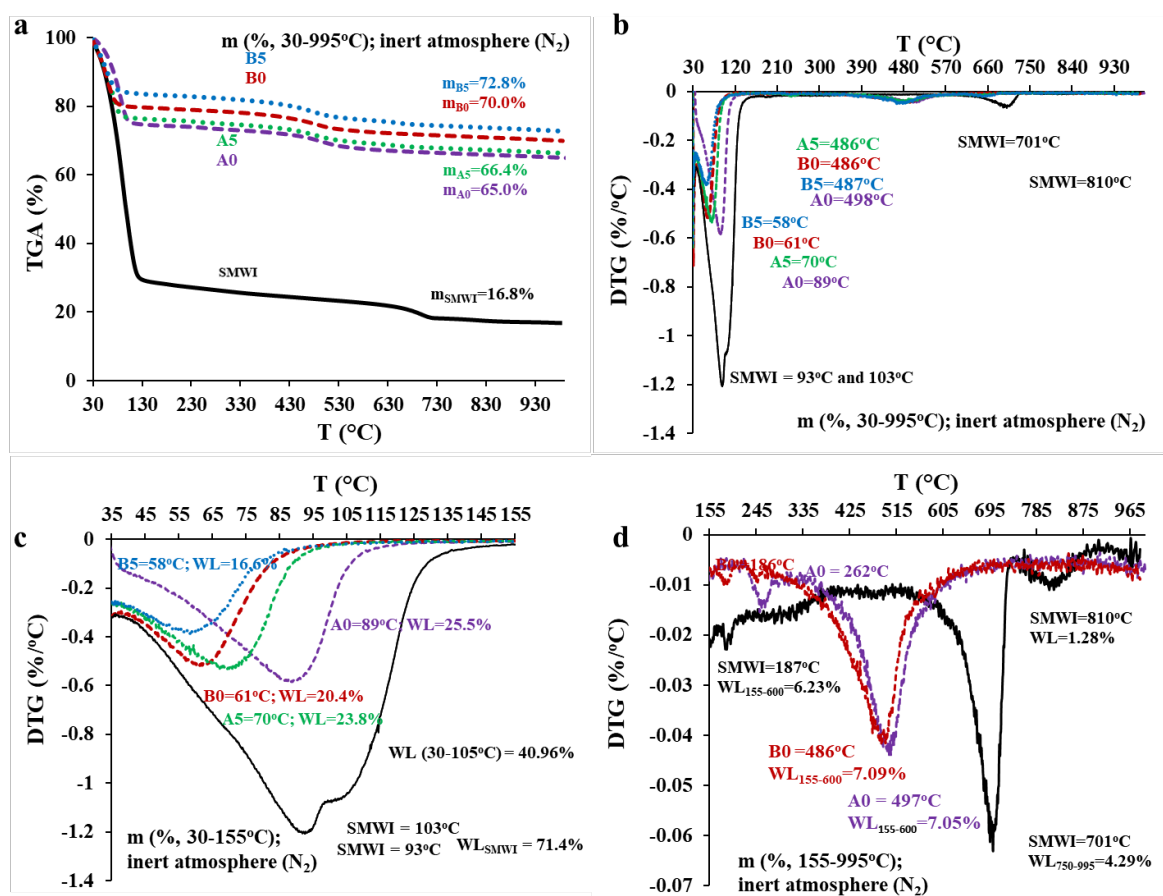


Figure 4: Evolution of mass losses (WL) by TGA of SMWI and donated clays (A0 and B0) and additives at 5% with SMWI (A5 and B5) (a) and derivative curves for temperatures between 30°C and 995°C (b), 30°C and 155°C (c) and 155°C and 995°C (d).

Table 5: Evolution of mass loss (%) of SMWI and clays by TGA

Sample	30-155°C	155-600°C	600-750°C	750-950°C	950-990°C	30-995°C	Residual
SMWI	71.36	6.23	4.29	1.15	0.13	83.17	16.83
A0	25.48	7.11	1.04	1.10	0.29	35.04	64.96
B0	20.43	7.09	1.02	1.23	0.26	30.02	69.98
A5	23.79	7.05	1.39	1.17	0.22	33.62	66.38
B5	16.59	7.52	1.59	1.25	0.26	27.20	72.80

Note: SMWI samples A0 and B0 were *in natura*. A5 and B5 received dry SMWI to make up 5% (on a dry basis).

Notably, Al_2O_3 can react with silica at vitrification temperatures (1000-1650°C), forming mullite ($1.4\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) (Lima et al., 2022), which enhances the mechanical strength of ceramic materials (Muñoz Velasco et al., 2014; Ukwatta; Mohajerani, 2017), thereby offering new opportunities for incorporating SMWI into other ceramic products. Similarly, CaO can contribute to increased mechanical strength if it forms bonds with SiO_2 (Muñoz Velasco et al., 2014; Rodrigues; Della Sagrillo; Reis, 2020). Additionally, the weight loss (WL) of 75.8%, corresponding to the moisture content in the characterization of the untreated SMWI (Table 2), was seen up to 450°C. However, this result should be interpreted with caution due to differences in analytical techniques and the potential volatilization of substances other than water (Bernal et al., 2017).

Peaks at 701°C and 810°C (Figure 4d) are attributed to the decarbonation of calcium carbonate (Munir et al., 2018; Yaras, 2020; Martínez-García et al., 2012; Boukili et al., 2021) and the formation of illite ($((\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}[(\text{OH})_2, (\text{H}_2\text{O})])$) using various oxides from SMWI (Findik; Akyol; Sari, 2014). Finally, the WL_{SMWI} between 105°C and 995°C (42.21%) was slightly higher than the loss on ignition (LoI) value of 39.53%, due to the inherent differences between the techniques and the varying atmospheres—oxidizing in LoI and inert in TGA (Bernal et al., 2017).

The WL of A0 up to 155°C was higher than that of B0, which are both ready-to-use clays, showing distinct properties such as differences in organic matter content and water retention capacity (Dondi; Raimondo; Zanelli, 2014). The WL for additive clays (A5 and B5) was slightly lower (Table 5) than for the donated clays (A0 and B0), possibly due to the addition of dry SMWI. The first peak for B0 occurred earlier (61°C) than for A0 (89°C) (Figure 4c), and the additive forms shown even earlier peaks ($\text{WL}_{\text{B5}}=58^\circ\text{C}$ and $\text{WL}_{\text{A5}}=70^\circ\text{C}$) compared to their matrices (A0 and B0). The WL between 155°C and 600°C was similar for A0 and B0, slightly higher than for A5 and B5, consistent with the lower WL_{SMWI} . Peaks occurring between 450°C and 600°C (Figure 4d) in the donated and additive clays are associated with the dehydroxylation of clay minerals (loss of structural water), such as kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) dehydroxylation between 400°C and 650°C (Ptáček et al., 2014), and the decomposition of organic matter (Ukwatta et al., 2015; Zhang et al., 2016).

In this context, the thermostability of the donated clays mixed with 5% SMWI (A5 and B5) aligns with the formation of thermostable clay minerals in ceramics, highlighting the potential of SMWI as a beneficial additive in ceramic materials.

3.6 Microstructural and micro-composition analysis of SMWI and clays

The microstructure of the SMWI sintered in TGA (Figure 5a) showed a surface characterized by larger cracks and pores compared to those saw in A0 and B0. This appearance is expected due to the substantial amount of water randomly distributed among the particles, which is removed during sample preparation. In contrast, the relatively uniform appearance of A0 and B0 (Figures 5b and 5c) can be attributed to their prior preparation for red ceramic production, resulting in more homogeneous masses.

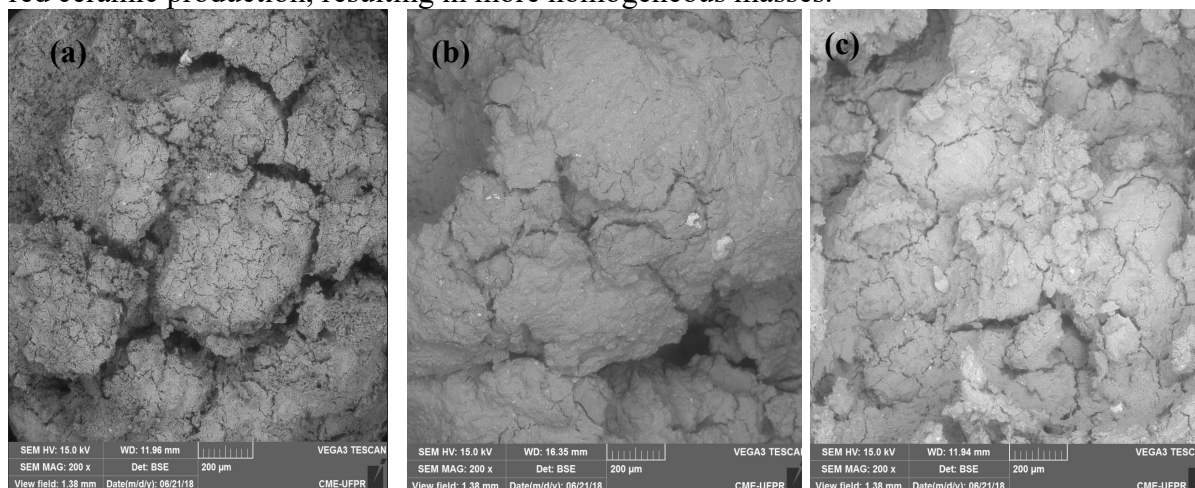


Figure 5: Images of SMWI (a), A0 clay (b), and B0 clay (c) by SEM.

Energy-dispersive X-ray spectroscopy (EDS) analysis of the SMWI (Table 6) revealed elevated levels of oxygen (23.4%) and carbon (36.7%), due to the presence of oxides and carbonates, as reported by Vieira and Silva (2012). The carbon content in SMWI was comparable to that of A0, while the oxygen content was like that of both B0 and SMWI. When comparing the composition using oxide equivalents, Al_2O_3 and CaO are predominant in SMWI. However, discrepancies between analysis methods were noted (Table 7), particularly when comparing results from EDS and wavelength-dispersive X-ray fluorescence (WD-XRF). For instance, CaO content was measured at 43.04% by WD-XRF, but 51.70% by EDS, a 20% increase in the latter. Similarly, discrepancies were seen for other elements, with EDS showing higher values for Fe_2O_3 and SiO_2 and lower values for Al_2O_3 and K_2O . The most significant discrepancy was for TiO_2 , where the EDS value was 207% higher.

Table 6: Average (n=5) proximate chemical composition of SMWI and clays by EDS during SEM

Sample	Si	Al	Fe	Ca	K	Ti	Mg	Na	P	C	O
SMWI	2.20	7.80	0.60	23.60	0.30	0.20	1.30	0.30	1.90	23.4	36.7
A0	16.00	11.10	4.50	0.20	0.80	0.60	0.30	ND	ND	24.0	42.5
B0	27.10	9.40	4.70	0.10	0.60	0.50	0.20	ND	ND	18.8	38.4
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	TiO ₂	MgO	Na ₂ O	P ₂ O ₅		
SMWI	8.78	23.07	1.34	51.70	0.57	0.52	3.38	0.63	6.82	0.00	0.00
A0	53.17	32.58	9.99	0.43	1.50	1.56	0.77	ND	ND	0.00	0.00
B0	68.49	20.98	7.94	0.17	0.85	0.99	0.39	ND	ND	0.00	0.00

Note: ND = not detected. The conversion of elemental values into their respective oxides was carried out using the atomic weight of the ChemicalAid (<https://www.chemicalaid.com/>) and the O and C values were purged to make up 100% of matter.

Table 7: Relationship between the average approximate chemical composition (n=5) of SMWI and clays by EDS during SEM and the chemical composition of SMWI and clays by WD-XRF

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	TiO ₂	MgO	Na ₂ O	P ₂ O ₅
SMWI	1.21	0.89	2.03	1.20	0.15	3.07	1.36	0.35	1.03
A0	0.85	1.23	1.42	1.98	1.22	1.00	1.38	ND	ND
B0	1.04	0.84	2.13	0.37	0.54	0.58	0.70	ND	ND

Note: ND = not detected.

These discrepancies are also clear in the analysis of A0 and B0 (Table 7), likely due to the heterogeneity of the samples analyzed by EDS. The variation in the analyzed fields becomes clearer when the analyzed points are magnified, revealing particles that are the overall sample composition (Table 8). It is important to note that these clays, despite being considered suitable for industrial use, are still fragmentary and heterogeneous. For example, the Ti content in A0 ranged from 0.4% to 2.1%, and in B0, it ranged from 0.4% to 15.4%. While this variation is less pronounced for major elements, it is significant enough to affect the reliability of the analysis under the conditions used.

Table 8: Spot chemical composition of clays by EDS during SEM

Sample	Point	O	C	Si	Al	Fe	Ca	K	Ti	Mg
A0	P1	35.9	36.1	9.6	9.3	5.4	0.3	0.5	1.2	0.2
	P2	36.7	31.2	13.2	9.6	7.3	0.1	0.8	0.8	0.2
	P3	20.4	26.3	8.9	7.0	36.5	0.2	0.4	0.4	0.2
	P4	45.0	15.0	18.4	12.3	6.1	0.1	0.6	2.1	0.3
	P5	44.2	12.7	14.4	11.8	15.6	0.2	0.5	0.6	ND
	P6	38.4	18.8	27.1	9.4	4.7	0.1	0.6	0.5	0.5
B0	P1	43.5	6.5	11.7	7.8	13.8	0.2	0.3	15.4	0.3
	P2	49.4	9.2	24.4	12.1	1.8	0.2	1.8	0.4	0.3
	P3	43.3	10.8	18.6	11.0	8.5	0.2	3.0	1.4	2.8
	P4	47.3	8.7	24.8	14.5	2.6	0.4	0.7	0.6	0.4
	P5	48.5	12.4	19.6	14.7	2.4	ND	0.9	0.6	0.4
	P6	47.3	11.3	22.6	14.3	2.4	0.4	0.6	0.6	0.6

Note: ND = not detected.

To improve precision and reliability, samples should be ground into exceptionally fine particles ($< 2 \mu\text{m}$) to complement X-ray diffraction (XRD) results (Clayton; Pearce, 2007). In this context, WD-XRF results should be considered more reflective of the actual composition of SMWI, A0, and B0 (Gazulla Barreda et al., 2016). It is also important to note that while WD-XRF provides elemental data on the chemical composition without differentiating between specific chemical compounds, XRD names and quantifies the minerals and their phases, offering a more comprehensive analysis of the sample's composition and structure (QUANTUM ANALYTICS, 2024).

4 Conclusions

This study evaluated the potential of using metallurgical sludge from the metalworking industry (SMWI) as an additive in clays used for brick production. For this purpose, SMWI and two industrial clays prepared for brick manufacturing were characterized thermally, chemically, and microstructurally. This innovative study conducted a detailed analysis of the generation, treatment, and composition of SMWI, proving its viability as an additive in ceramic production. Quantitative chemical analysis confirmed that SMWI is predominantly inorganic, containing components such as Si, P, Zn, K, Fe, Mg, Ti, Na, Cl, Al, and Ca, derived from the pretreatment and surface washing of metal parts and the reagents used in the Effluent Treatment Plant (ETP). Although SMWI does not exactly match the composition of sewage and industrial sludges typically used in ceramics, its composition rich in SiO_2 , Al_2O_3 , Fe_2O_3 , and CaO makes it suitable to produce both red and white ceramics. The high CaO content can enhance the mechanical strength of ceramics, though excess CaO could reduce strength and increase water absorption. The SiO_2 in SMWI mitigates these effects, but its addition should be limited to around 5% by mass. Utilizing SMWI as a ceramic raw material enables the immobilization of pollutants within the ceramic matrix or their thermal degradation during manufacturing. For efficient production, SMWI must be adequately

fragmented and mixed, ensuring a homogeneous mass despite the anisotropy of the particles. Therefore, substituting clay with SMWI in brick manufacturing presents a promising alternative for waste valorization and reducing the environmental impact associated with clay extraction. Further studies are recommended to evaluate the physical and mechanical properties of ceramics produced with this residue to ensure their technical feasibility according to Brazilian standards.

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