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Ca₂V₂O₇ as an Anode-Active Material for Lithium-Ion Batteries: Effect of Conductive Additive and Mass Loading on Electrochemical Performance

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Lithium-ion batteries (LIBs) play a crucial role in using renewable sources. Vanadates have been applied as anode material due to the combined diffusion mechanisms and higher and stable capacities. Despite the interest in vanadates as anode materials, only a few studies have considered Ca₂V₂O₇ (CVO) as an active material for LIBs. This work focuses on the use of CVO as a potential alternative anode-active material for LIBs. Additionally, we investigate the effect of the conductive additive (C65) on the electrochemical properties of the electrodes, utilizing densified electrodes with a porosity of about 40%. In doing so, this study provides important insights into new

materials for LIBs, where the electrodes were manufactured using the commercial slurry methodology, replacing graphite by CVO – which was synthesized via the Pechini route (D50: 8 μm after milling). In summary, the results reveal that the amount of C65 positively affects the electrode's capacity. An increase in specific capacity was observed by up to 30% using 10 wt.% C65. Such electrodes showed 235 mAh/g_{AM} at C/10 and, when cycled at 1 C, completed 300 cycles with a retained capacity of 39%. The results demonstrate that CVO might be a promising anode material for LIB energy storage systems.

Introduction

Recently, there has been a growing demand for renewable energy. Since natural sources such as wind and solar irradiation do not produce energy continuously, efficient energy storage systems are required, and lithium-ion batteries (LIB) have become one of the most powerful technologies in this field.^[1]

Most LIB electrodes, not only for industrial production but also for research purposes, are manufactured via the slurry methodology.^[2–5] In this sense, the binder system is a crucial

point that should be taken into account during the electrode manufacturing step, as it is responsible for guaranteeing a homogeneous dispersion of the components in the slurry, attaching the particles to the current collector, tolerating dimensional changes during charge and discharge, and remaining chemically and electrochemically stable during the process.^[6]

Furthermore, the aqueous system containing the CMC/SBR binder has the advantage of producing batteries with less environmental impact, lower production costs regarding solvent recovery, and a high production rate.^[1,5,7] Graphite has been the anode-active material used in commercial LIBs for the past 30 years due to its high specific capacity of 372 mAh/g and Coulombic efficiency.^[8,9] However, it can have the structure destroyed during the charge/discharge process.^[10,11] Additionally, safety problems caused by dendrite formation during cycling are reported. Thus, searching for novel anode materials with high electrochemical performance is an ongoing task.^[12]

Numerous vanadium oxides have already been studied as potential anodes for LIBs, such as MV₂O₄,^[13,14] MV₂O₆,^[15,16] MV₂O₇,^[17–21] MV₂O₈,^[22,23] for different reasons. One reason is that the vanadium element possesses several valence states and can form various structures, leading to rich Li⁺ storage.

The lithium storage mechanism can be divided into intercalation (e.g., graphite^[24,25]), conversion (e.g., transition metal oxides, metal sulfides, phosphides^[26,27]), and alloying (e.g., Si, Zn, Sn oxides – CaSnO₃^[28,29]), depending on the interaction between those materials and the lithium element.^[28,30] Vanadates present combined mechanisms providing large and stable capacities, usually composed of general conversion reactions, commonly reversible,^[11] where the reduction of V ions to a lower valence state (e.g., V⁵⁺ → V⁴⁺) accompanies the incorpo-

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ration of lithium ions (reversible after the delithiation).^[11,26] Meanwhile, vanadates can also accommodate the local volume change during repeated Li^+ insertion/extraction and thus improve the cycling stability,^[31–33] as observed for $\text{Co}_2\text{V}_2\text{O}_7$.^[15,18,33]

Cobalt-vanadates exhibit one of the best performances and highest capacities observed for this material class, reaching more than 1000 mAh/g.^[34–36] However, cobalt is toxic during all stages of the battery manufacturing process and has an expensive and challenging supply.^[37–41]

For the reasons mentioned above, calcium pyrovanadate (CVO) could be an alternative since calcium and vanadium are nontoxic in standard concentrations and abundant on Earth^[42] – and possess a layered framework with a triclinic structure. Even after studying for years since 1981,^[20,43–49] the application of CVO as a component in LIBs is still not widely exploited.

The published work from Zhang and Mu^[20] studied the electrochemical performance of CVO as anode-active material in LIBs, using acetylene black as a conductive additive and a PVDF binder system; the electrochemical performance showed a capacity of 547.5 mAh/g and 296.0 mAh/g for the first and second cycles, respectively.

The work presented in this study aims to investigate $\text{Ca}_2\text{V}_2\text{O}_7$ (CVO) as an anode-active material for conventional LIB in a water-based binder system utilizing SBC/CMC binder system and to build up chemically stable and cyclable cells. To this end, we combined microstructural and electrochemical investigations to better understand the mechanisms behind this material as an anode for LIB.

Results and Discussion

Several analyses have been carried out to understand the behavior of CVO as an anode material in the conventional LIB system and the effect of conductive additives and densification on the electrochemical properties.

Figure 1(a) shows the typical XRD pattern of the synthesized CVO powder. All diffraction peaks were identified as mono-phasic pure $\text{Ca}_2\text{V}_2\text{O}_7$ (JCPDS 01-072-2312), and the Rietveld parameters are described in Table 1.

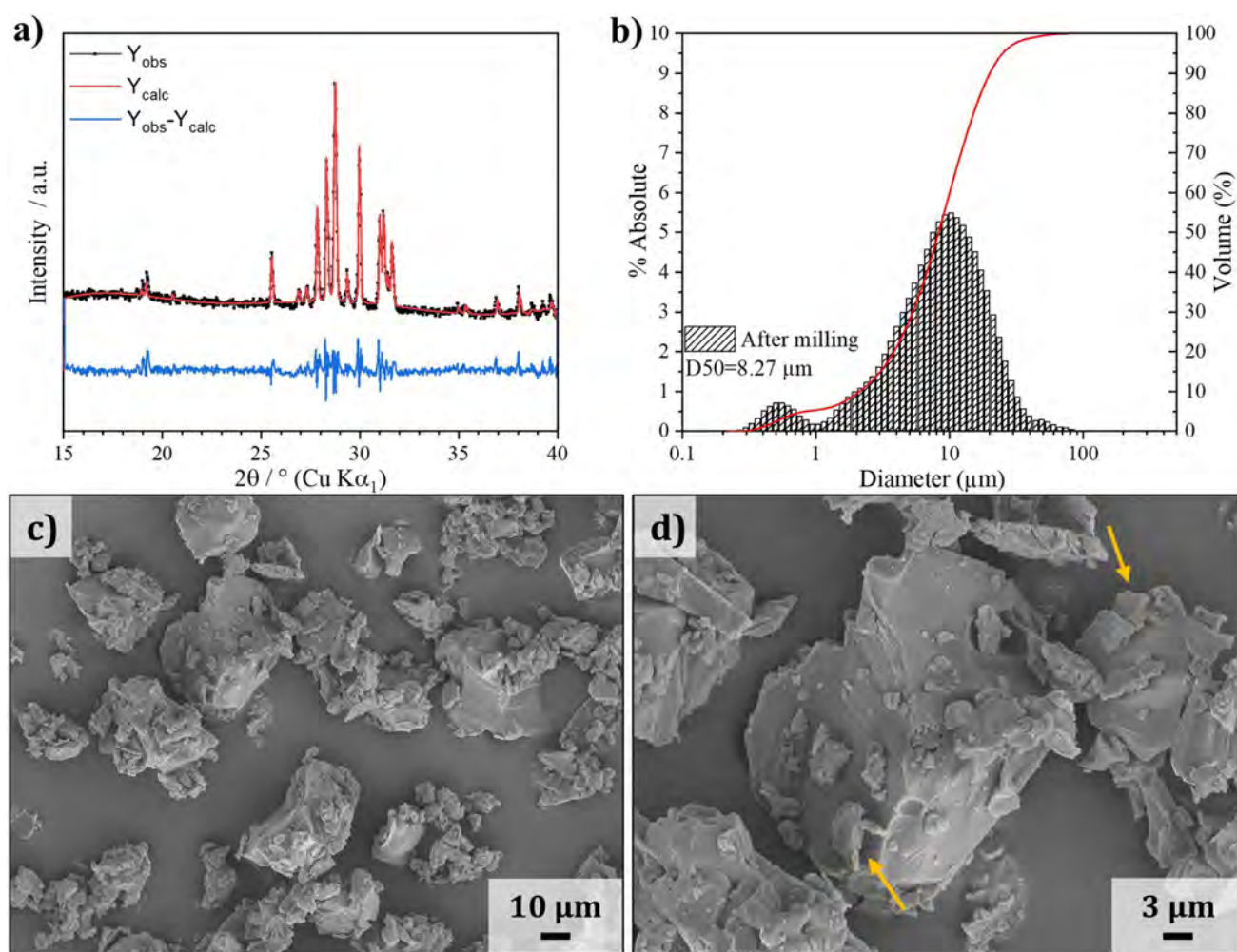


Figure 1. (a) XRD patterns of the CVO powder synthesized by the Pechini method, (b) particle size distribution, and (c,d) SEM image of the milled powder (small particles in yellow arrows).

Table 1. Refinement parameters and crystallographic data of $\text{Ca}_2\text{V}_2\text{O}_7$.			
	Present work	[48]	[49]
Symmetry	Triclinic		
Space group	$P\bar{1}(2)$		
a (Å)	6.62	6.67	6.68
b (Å)	6.88	6.93	6.92
c (Å)	6.97	7.02	7.02
α (°)	86.40	86.45	86.44
β (°)	63.87	63.83	63.86
γ (°)	83.63	83.71	83.69
volume (Å) ³	283.66	–	289.04
Rwp (%)	5.96	–	7.73
Rexp (%)	2.80	–	–

Figure 1(b) shows a bimodal particle size distribution of the milled CVO powder and presents a population of small (0.5 μm) and big particles (10 μm). The observed D50 was 8.27 μm .

Figures 1(c) and (d) show the SEM images of the CVO powder indicating a single crystalline morphology and confirm the particle size measurements. The bimodal distribution provides better particle packing in the electrodes (small particles attached to the bigger ones are marked with a yellow arrow).

According to the refinement applied, the CVO has a triclinic structure, with $P\bar{1}(2)$ space group symmetry, and lattice parameters similar to those observed in previous work.^[48,49] The observed Rwp is around 5.96%, while Rexp is 2.80%, generating a GOF of 2.12; some authors explain a GOF above one as a minor systematic error in the data, such as the background effect.^[50,51]

Figure 2 displays representative top-view SEM images of the surfaces of the electrodes with different C65 content. The increasing amount of C65 can be seen in Figure 2, where the carbon-binder domain (CBD) is marked with red arrays. In all samples, the CVO particles are dispersed rather homogeneously within the CBD. Note that the CVO particles partially exhibit cracking due to the mechanical loading during compaction.

The cross-sectional SE images of the samples confirm above mentioned findings, which can be seen in Figure 3. The images explicitly reveal the homogeneous distribution of CVO particles throughout the thickness of the electrode as proof of a successful manufacturing methodology. Moreover, the reduced amount of CVO can be observed clearly comparing Figure 3(a, c and e). Again, it can be observed that the CVO particles are broken due to the densification step. Note, that in the cross-sectional view, dark gray and black areas represent both the porosity and the CBD phase since they cannot be distinguished in the SEM BSE (back-scattered electron) images.

The electrochemical performance of the CVO electrodes was tested using various electrochemical techniques. In this work, the charge is defined as when the Li^+ is diffused into the CVO structure, and discharge is defined as when the Li^+ departs the CVO.

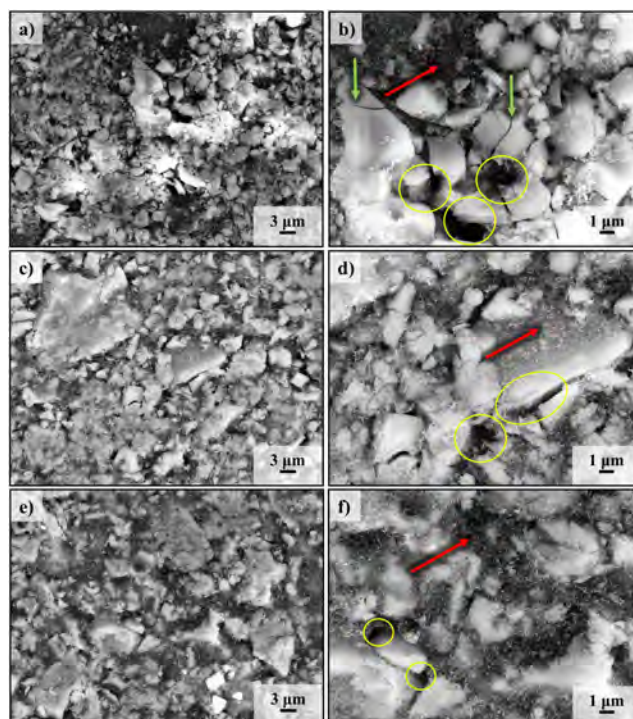


Figure 2. Top view SEM images of the surface of the electrodes using SE (secondary electron) detector: CVO2 (a,b), CVO5 (c,d), and CVO10 (e,f) (C65 + binder region in red arrows, pores in yellow circles and cracks in green arrows).

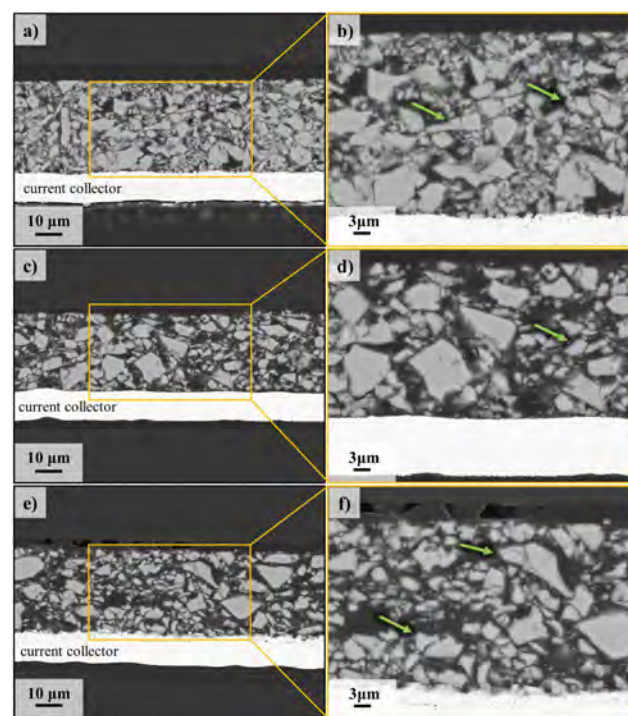
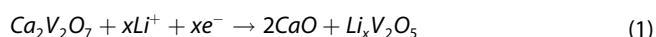


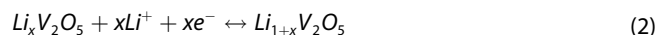
Figure 3. SEM BSE images of the cross-section of the electrodes: CVO2 (a,b), CVO5 (c,d), and CVO10 (e,f) (mechanically-induced cracks due to densification step in green arrows).

Figure 4(a) shows exemplary cyclic voltammogram (CV) curves for CVO10. The first cycle indicates a different behavior during lithiation but the same behavior during delithiation compared to subsequent cycles. During the delithiation process, a peak was observed starting at 0.604 V, with a maximum at 1.03 and ending at 1.38 V. Two different reduction sweeps are observed at 0.963 and 0.633 V in the lithiation step for cycles 2 and 3.

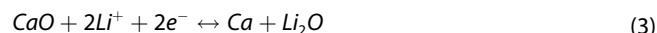
The difference in the cathodic sweeps between the first and the second cycle could be related to the different lithiation processes during the first charging step. The reduction peak starting at 1.13 V in the first cycle might be due to the decomposition (irreversible) of CVO into $\text{Li}_x\text{V}_2\text{O}_5$, as described in Equation 1.



As the voltage decreases, the cathodic scan displays a strong peak centered around 0.040 V that could be associated with the uptake of additional Li^+ into $\text{Li}_x\text{V}_2\text{O}_5$ depth; this process usually results in the formation of the SEI layer, as expressed in Equations 2 and 3.



and



In the second and third cycles, differences for the first lithiation are observed at two peaks at 0.633 V and 0.963 V, which could be the accommodation of Li^+ in $\text{Li}_x\text{V}_2\text{O}_5$, as previously described in Equation 2, and possibly the oxidation of the vanadium atom from V^{5+} to V^{3+} , usually observed at 0.668 V.^[52] Similar behavior is described by Sambandam and Wang in $\beta\text{-Mn}_2\text{V}_2\text{O}_7$ and $\text{Cu}_2\text{V}_2\text{O}_7$, respectively.^[17,53]

The anodic sweeps show an unchanged broad maximum between 0.604 and 1.38 V centered at 1.03 V and a small hump at 1.62 V, which could be interpreted as the extraction of Li^+ from the $\text{Li}_{x+y}\text{V}_2\text{O}_5$ matrix (Equation 4) - together with vanadium oxidation from V^{5+} to V^{4+} at 1 V, as described in.^[53]

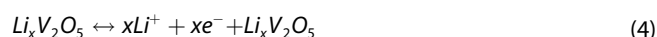
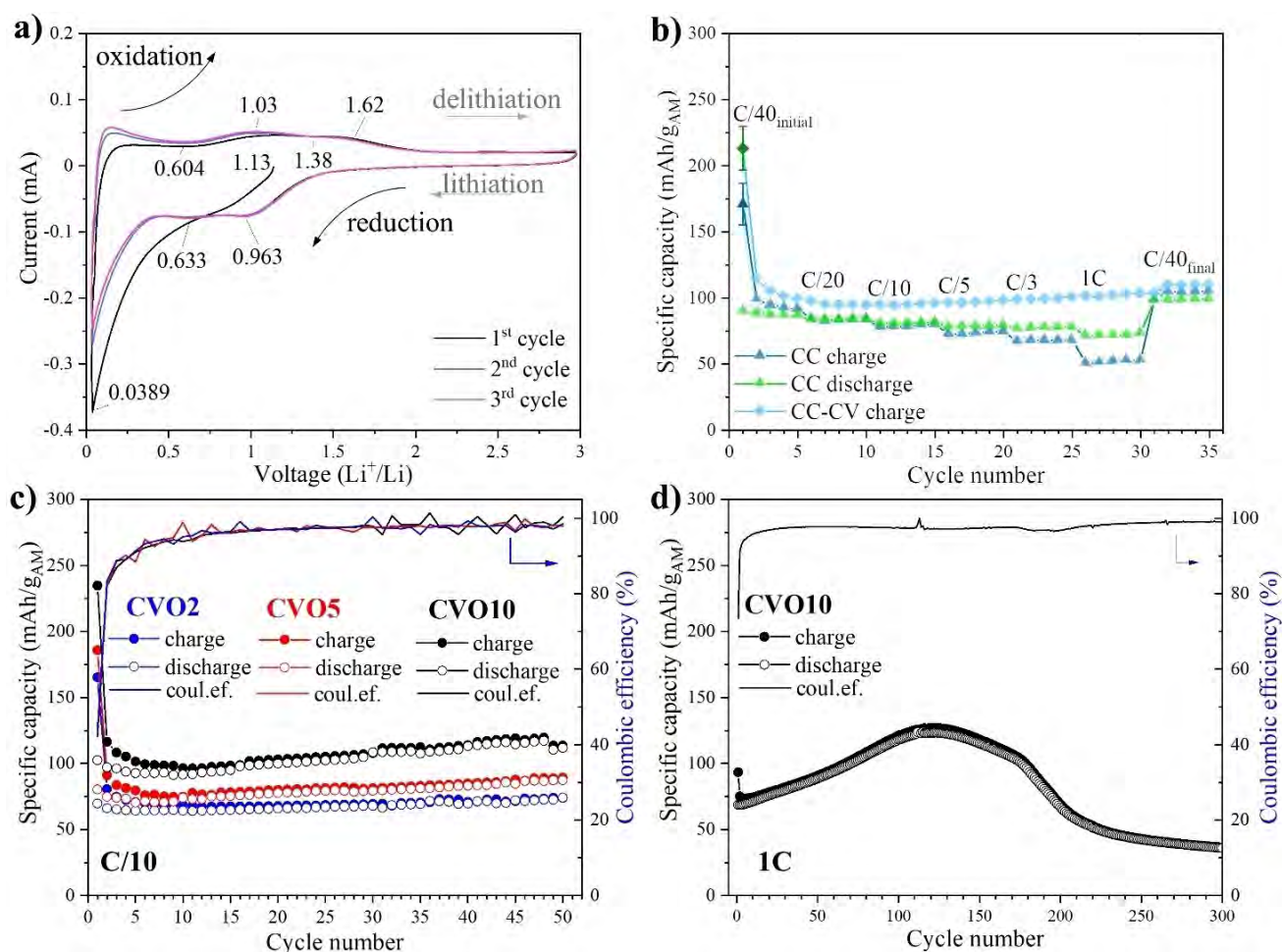


Figure 4. Electrochemical evaluation of CVO for LIBs: (a) cyclic voltammogram (CV) curves for electrode CVO10, (b) rate capability at several C-rates for electrode CVO10, (c) cycling performance at C/10 for electrode CVO2, CVO5, and CVO10, (d) long-term cycling at 1 C for electrode CVO10 after 3 formation cycles at C/10.

CVO exhibits stable capacities after the first cycle at different C-rates shown in Figure 4(b). At CC–CV mode, the CVO10 electrode showed constant charge capacities (after the very first capacity drop) of 114 mAh/g_{AM} at C/40_{initial}; even at 1 C, this electrode delivered a specific capacity of 103 mAh/g_{AM} during charging. At C/40_{final}, a capacity of 110 mAh/g_{AM} is observed, slightly higher than observed for the first five cycles (C/40_{initial}), suggesting that CVO presents excellent stability. Figure 4(c) shows that the C65 ratio significantly affects the initial specific capacity. Increasing the amount of C65 from 2 to 5 wt% and 5 to 10 wt% results in a capacity gain of 21.4 mAh/g_{AM} (11%) and 48.1 mAh/g_{AM} (20%), respectively (compared to the first charge capacity). This effect can be very likely attributed to the improved electronic conductivity with the increasing amount of C65.

A substantial charge capacity drop within the first three cycles is observed for all samples, whereafter 41% of the initial charge capacity remains, with the most significant portion attributable to the first cycle. However, the capacity stabilizes after a few cycles and slowly recovers within continuous cycling. After 50 cycles, the retained reversible capacity is around 50% of the initial charge capacity for all samples (see Table S4 in Supplementary Information), coinciding with an increase in the Coulombic efficiency, which is approximately 95% and stable after 10 cycles.

Following Ref.^[17,54,55] the substantial decrease in capacity observed in the first cycles occurs due to the consumption of lithium ions as a result of the irreversible phase transition ($M_xX_y + zLi^+ + ze^- \leftrightarrow xM + Li_zX_y$), which was previously detected in CoV₂O₆^[17,54,55] and Mn₂V₂O₇.^[17,21,56] However, other authors claim that the capacity drop occurs due to SEI formation when the decomposition of the organic electrolyte is thermodynamically favorable at potentials below 1 V (versus Li/Li⁺)^[57] as observed in Co₂V₂O₇,^[18,33] Cu₂V₂O₇,^[58] and Zn₂(OH)₃VO₃.^[59] Nevertheless, the authors note that the SEI layer could not be seen by SEM imaging techniques which are confirmed in our study.

To further evaluate the cycling stability of the CVO electrodes, the long-term aging behavior of the CVO10 electrode was investigated by performing 300 cycles at 1 C, carrying out the initial three cycles at C/10 for the formation of the SEI layer (Figure 4d). CVO10 shows a significantly lower capacity than was observed at C/10. Again, we observe a decreasing capacity within the first few cycles, starting from 93 mAh/g_{AM} (first cycle) to 73 mAh/g_{AM} after the 5th cycle (21.4% of capacity loss), followed by a remarkable recovery process. However, when the highest capacity of 127 mAh/g_{AM} in the 123rd cycle is observed, a downward trend begins. In the last cycle (300th), the charge capacity was 36 mAh/g, corresponding to 38.9% of retained capacity (all data in Table S5 in Supplementary Information).

The lower capacity related to cycling at 1C is explained by,^[60] where higher C-rates require higher porosities.

A comparable behavior, i.e., a significant capacity recovery during cycling, has previously been reported for metal oxides, most often for 3d metal oxides (Co, Cu, Ni, Fe, and Mn), where it was suggested that during the formation of the SEI layer, metal particles (usually nanosized) are formed.^[27,61] These particles are

kinetically activated by electrolyte decomposition, creating a gel-like polymer film (PGF) and providing additional Li⁺ storage at the interface.^[19,34,36,62] Some studies^[23,63,64] mentioned that these nanoparticles could increase the electrode's overall conductivity and improve charge transfer kinetics, resulting in increased capacity in subsequent cycles. Increased capacity from 10 to 80%, which is often observed in long-term cycles (N > 100), can also be associated with the gradual activation of vanadium-based electrode materials (i.e., During lithiation/delithiation, the active material particles break into several pieces, those pieces become available for new electrochemical reactions).^[14,34–36]

The observed capacity fade after achieving the maximum capacity (which can be interpreted as the maximum activation of the CVO) is also described for other vanadates in LIB.^[23,33,65] The authors claim that this phenomenon can be attributed to the vanadates' activation process, which takes place over many cycles. This subsequent activation overshadows the potential degradation of already activated CVO. However, after all of the CVO is activated, its subsequent degradation due to cyclic charging/discharging becomes visible.

To better understand this behavior, post-mortem analyses via XRD was performed on the CVO10 electrodes after 300 cycles (Figure 5).

After cycling, the XRD shows that the CVO is still present in the electrode material. In addition, new phases, for example, V₂O₁₃ (COD 96-153-0104), CaO (COD 96-900-6746), and LiOH (COD 96-900-8959), are identified. Note that the peak at 2-theta = 30° representing the (200) plane in the CVO electrode is more intense after cycling. This peak could also be attributed to V₂O₁₃ due to the decomposition of the CVO phase. The new phases identified in the electrode after cycling evidence the reactions described during the cyclic voltammetry (see Figure 4a). For example, during the first lithiation, CVO decom-

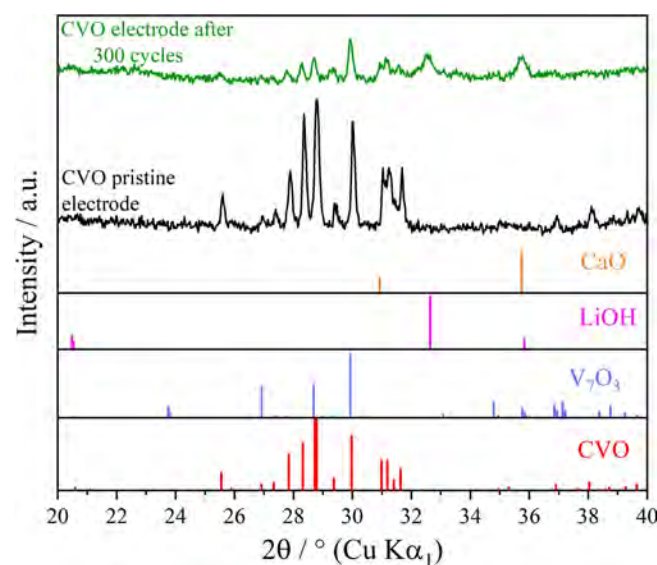


Figure 5. Post-mortem analysis of cycled electrodes: XRD pattern of pristine and cycled CVO10 electrode.

poses in CaO and $\text{Li}_x\text{V}_2\text{O}_5$ (according to the chemical reaction expressed by Eq. 1).

LiOH most probably comes from the decomposition of the lithium metal under air or the liquid electrolyte. However, phases such as Li_2O and $\text{Li}_x\text{V}_2\text{O}_5$ could not be identified, which might be due to shading from the other more intense peaks or the limited amount. Besides, Li_2O and $\text{Li}_x\text{V}_2\text{O}_5$ can occur as amorphous phases, as previously reported,^[17,33,58] thus being invisible for XRD.

The microstructure of the CVO10 electrodes was analyzed after 300 cycles to understand better the effect of charge/discharge cycles on the morphology of the CVO particles (Figure 6).

When comparing the CVO particles before cycling and after 300 cycles, it becomes apparent that the amount of cracks has increased (as depicted in Figure 3e and f). However, the ability to quantify this increase remains limited.

In Figure 7, a scheme is proposed to illustrate the behavior of $\text{Ca}_2\text{V}_2\text{O}_7$ particles during cycling. It is believed that creating freshly exposed surfaces caused by microcracking enhances electrochemical activity.

Before cycling ("fresh cell"), the CVO particles within the freshly prepared electrodes present mechanically induced cracks as a result of the densification step (see Figure 2b and 3f). The cracks within the CVO particles begin to proliferate with the first charge/discharge cycle. Subsequently, throughout the cycling process, the CVO particles undergo further cracking, leading to the generation of numerous smaller fragments,

improving the contact between the active material and the liquid electrolyte.

These fragmented particles are electrochemically activated, i.e., they exhibit fresh surfaces promoting the electrochemical reactions. This in turn, contributes to an increase in capacity over successive charge/discharge cycles. At the same time, the newly created surfaces promote parasitic side reactions that consume electrolyte and result in the growth of surface layers (SEI) and, thus, an increase of the internal resistance.^[66] Both processes have an opposite effect on the cell performance. However, the experimental findings suggest that the fragmentation process saturates at a certain stage of cycling, indicating that maximum capacity has been reached (in the present work, 123rd cycle). Until that critical point, the promotion of the electrochemical reactions due to fragmentation overshadows the negative effect of the side reactions. Nevertheless, beyond this critical point, the parasitic side reactions dominate the overall performance of the electrode. Consequently, as the cycling process continues, a noticeable decline in capacity becomes evident, signifying a progressive deterioration in overall performance.

Work in similar materials has also reported activation process; however, the authors never explain in detail the mechanism.^[34,35,58,59,67]

Nonetheless, compared to the work of Zhang and Mu,^[20] the specific capacity overall in this study is about 50 % lower. Most likely, the difference is due to the CVO powder synthesis route and particle design.

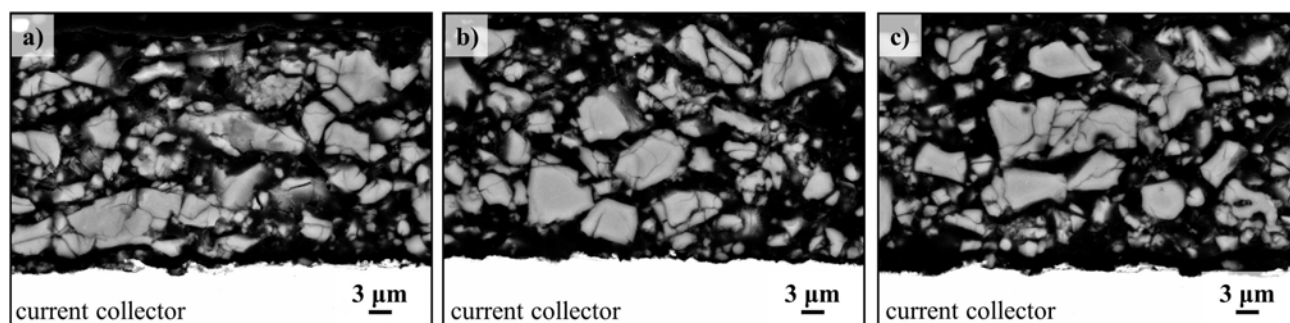


Figure 6. SEM BSE images of the cross-section of the electrode CVO10 after 300 cycles in different regions.

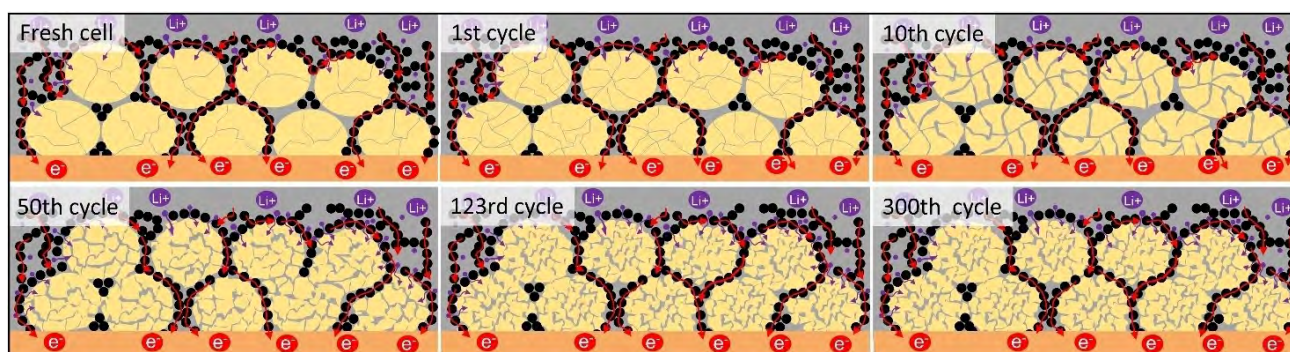


Figure 7. Lithiation and activation process during cycling for $\text{Ca}_2\text{V}_2\text{O}_7$.

Conclusions

This paper shows the application of CVO, which was synthesized via the Pechini method as an anode in LIB, and investigates the effect of the conductive additive content on their electrochemical properties. By combining microstructural and electrochemical characterization methods, the work provides new insights into CVO as anode active material and shows that CVO can be processed using water-based CMC/SBR binder systems, providing benefits for environmental compliance and costs.

Cyclic voltammetry test and X-ray diffraction reveal the multi-step reaction of CVO during charge/discharge similar to comparative materials.

The electrochemical investigations evidenced that the battery capacity is strongly related to the amount of the conductive additive. It is shown that (i) the higher the quantity of C65, the higher the specific capacity of the batteries – most likely due to the poor conductivity of CVO.^[48] In this way, C65 is required to build the conductive network (ii) the applied C-rate influences the battery capacity and should be considered during the electrode design since higher C-rates require higher porosities.

Recovery behavior could result from the reactivation of the CVO particles due to volume change during the lithiation/de-lithiation process, leading to cracks through the CVO particles and providing new surface areas for the electrochemical reaction.

The mechanical densification, as well as cyclic charging/discharging, promote cracking on the CVO particles, which is beneficial for the electrochemical reactions since the CVO active surface is increased. A finer particle and surface coating could certainly enhance the electronic conductivity of CVO-powder, as observed, i.e., for LiFePO₄.^[68] In parallel, however, side reactions occur at these surfaces, leading to a deterioration in electrode performance. Both mechanisms have opposite effects on cell performance and dominate the cell properties at different cycling stages.

Experimental Section

For the synthesis of CVO, the methodology developed by Maggio Pechini^[52,53] was chosen, as described in a previous study,^[69] where the calcination was performed at 900 °C for two hours with a heating rate of 10 °C/min to obtain the final product. The synthesized powders were milled in a planetary ball mill (Fritsch Pulverisette 5) using a nylon jar with yttrium-stabilized zirconia balls (NETZSCH 3 mm) in ethanol at 300 rpm for 15 min. The suspension was dried under infrared lamps (SCT E27R125 IR220/250) for 24 h.

The electrodes were prepared following the slurry methodology used in commercial lithium-ion batteries.^[70] Carboxymethyl cellulose (CMC, Nippon, Sunrose MAC 800LC) and Styrene-Butadiene Rubber (SBR, Zeon, BM-451B) were utilized as binder system, and carbon black (C65, Imerys, C-Nergy Super C65) as a conductive additive to prepare the active mass together with the synthesized CVO (formulations and final characteristics of

the slurries are shown in Table S1 and S2 – Supplementary Information).

The CMC was dissolved in deionized water and added under mechanical agitation (dissolver Hei-TORQUE 400, HEIDOLPH) at 2000 rpm, followed by adding C65. After 24 h under 2000 rpm, CVO and SBR were added to the mixture. The slurry was coated on copper foil (thickness: 10 µm) and dried under air for 24 h. Then, the electrodes were uniaxially pressed at 280 MPa to reduce porosity and ensure mechanical stability as described by.^[60] Finally, CR2032 coin-type cells were assembled in an argon-filled glovebox using lithium foil (Thermo Scientific, thickness: 0.75 mm, diameter: 14 mm) as a counter electrode, glass fiber GF/A (Whatman, diameter: 16 mm) as separator and a liquid electrolyte (Solvionic, 12.8 wt.% of LiPF₆, 25.56 wt.% of ethylene carbonate, 59.6 wt.% diethyl carbonate and 2 wt.% of vinylene carbonate). The specific capacity was calculated using the working electrode's active material (AM) content (Table S3 – Supplementary Information).

Three different ratios of conductive additive (C65) were used, 2 wt.%, 5 wt.%, and 10 wt.%, by keeping the amount of CMC and SBR constant but varying the amount of CVO accordingly. Table 2 summarizes the characteristics of each different formulation. The porosity was calculated as described in Eq. S.1. in Supplementary Information.

A series of analyses were performed to understand the mechanism of CVO in LIB. For the rate capability test, five cycles were performed for each C-rate (C/40, C/20, C/10, C/5, C/3, 1 C, and C/40 again). Two aging tests were carried out using a Basytec CTS Lab battery testing system in the voltage range of 0.01–3.0 V vs. Li/Li⁺ at room temperature in CC-CV mode, at C/10 for 50 cycles and 1 C for 300 cycles performing the initial three cycles at C/10 to establish a stable SEI layer.

All tests were performed in triplicate, and the specific capacity was calculated according to the mass of active material (CVO). The C-rate current was defined, assuming a specific capacity of 288 mAh/g according to Zhang and Mu.^[20] Charging was always done in CC-CV mode with a CV charging termination current of C/100 for every C-rate while discharging was done in CC mode only. The cyclic voltammetry (CV test) was performed using a potentiostat (BioLogic type VSP 300) in the voltage range of 0.01–3.0 V with a ratio of 0.1 mVs⁻¹.

The crystalline phases were characterized by X-ray diffraction (XRD) using Sun XRD 3003 equipment (SEIFERT Analytical X-Ray), with Cu-Kα radiation (λ = 0.15406 nm), monochromatic X-Ray source, operated at 35 kV and 50 mA. The analysis was conducted with a 2θ range of 10–70°, and a scan rate of 0.008 °min⁻¹. Rietveld refinement was carried out on the academic version of TOPAS software.^[71] Microstructural characterization was performed using a Zeiss Sigma 300VP scanning electron microscope (SEM) with secondary electron (SE) and back-

Table 2. Sample characteristics.

Component	Code	Thickness (µm)	Compaction degree (%)	Porosity (%)
Weight ratio (%)				
CVO C65 CMC SBR				
94 2 2 2	CVO2	35 ± 2.9	37.5	35
91 5 2 2	CVO5	30 ± 2.4	31.8	41
86 10 2 2	CVO10	28 ± 3.8	45.1	40
[*] Mean value and standard deviation, measured with 20 samples.				

scattered electron (BSE) modes. The particle size of the CVO powder after the milling process was evaluated using a laser scattering method on SALD-2201 (Shimadzu®) equipment in water at room temperature. Previously, the powder was dispersed in sodium hexametaphosphate 2 wt.% aqueous solution in a beaker applying ultrasound for 15 min.

Supporting Information

The authors have cited additional references within the Supporting Information.^[72]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: anodes · $\text{Ca}_2\text{V}_2\text{O}_7$ · lithium-ion batteries · pechini · transition metal oxide · vanadates

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Effect of synthesis method on the structural and optical properties of $\text{Ca}_2\text{V}_2\text{O}_7$

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Abstract

Vanadium oxides have been extensively studied once vanadium oxidation states provide unique characteristics, allowing applications in several areas, such as light-emitting devices and photocatalysts. The solid-state reaction is the oldest route for synthesizing ceramic compounds; however, it includes a lack of homogeneity and purity in the final material. In contrast, the Pechini method enables excellent particle size and morphology control, together with high-purity materials, at lower temperatures and reaction times. Although synthesis strongly influences the material's applicability, few studies have compared these methods experimentally. The present work expects to contribute to understanding the differences between solid-state reaction and Pechini routes in the obtention of CaV_2O_7 and how it impacts the final characteristics of the material. The synthesis was carried out using the solid-state method and modified Pechini in a temperature range of 650–850 °C. The powders possess a particle distribution as a function of temperature. The material shows an absorbing performance of about 500 nm, with a band gap of around 3 eV, slightly higher for the solid-state reaction route, as it is closely related to the size and purity of the particles. In summary, the results suggest that the solid-state reaction requires a higher temperature to obtain a higher purity material, while the Pechini method provides the same purity at all temperatures applied, together with a more homogeneous morphology, which shows to be a promising photocatalyst material capable of decolorizing 40% of a methylene blue solution in 120 min where it can play an important role for wastewater treatments.

Keywords $\text{Ca}_2\text{V}_2\text{O}_7$ · Pechini method · Solid-state reaction · Photocatalyst

Introduction

Along with the development of society, the insufficiency of natural resources is becoming more evident. In this way, the search for materials and treatments that allow wastewater utilization has been the focus of recent research. Many advanced treatments are based on photocatalyst materials, also known as semiconductors. These materials can decompose organic pollutants in water when excited with a radiation source [1–3].

Vanadium oxide-based materials have attracted particular attention because of their unique structural, optical, and

magnetic properties. It is known that vanadium oxide transforms into different complex vanadates, namely metavanadate, pyrovanadate, and orthovanadate, depending on the considered stoichiometry of the composition [4, 5].

These characteristics are related to the electronic configuration of vanadium [argon] $4s^23d^3$. This element is often found in oxides in all oxidation states that can be between +5 (d^0) and 3 (d^3) in an aqueous solution [6]. Pyrovanadates $\text{M}_2\text{V}_2\text{O}_7$ (M =equivalent element of the periodic table) when it is the alkali earth metal-based oxides $\text{A}_2\text{V}_2\text{O}_7$ (A =Ca, Sr, Ba, etc.) is of particular interest to investigate their intriguing correlations among crystal structure, electronic/atomic structure, and important application areas such rare earth element-free white light-emitting devices [7, 8], supercapacitors [9], photocatalysis [10–13], a cathode for zinc-ion batteries [14], components for lithium-ion batteries [15–17], and also in the field of health as detection of antibiotic drugs [18]. The pyrovanadates obey the triclinic crystal structure. They are generally prepared at lower sintering temperatures

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than conventional ceramic materials, consistent with the energy-saving requirements of products today.

$\text{Ca}_2\text{V}_2\text{O}_7$ and $\text{Ca}_2\text{V}_2\text{O}_7$ -based materials with different morphologies have been synthesized [8, 9, 19–21]. $\text{Ca}_2\text{V}_2\text{O}_7$ is one of the pyrovanadate minerals, consisting of a layered crystal structure similar to other metal vanadates. Some authors observed that $\text{Ca}_2\text{V}_2\text{O}_7$ microspheres have photoabsorption from UV light to visible light at about 470 nm, and the band gap value was 2.65 eV. The optical band gap value determined indicates that the $\text{Ca}_2\text{V}_2\text{O}_7$ microspheres show a semiconducting behavior essential for the UV-induced photocatalytic degradation of organic pollutants [20]. The synthesis process has a considerable influence on the material properties. It can determine the properties and application of these materials [22]. Most ceramic materials are still synthesized by the solid-state reaction, being the oldest and most used methodology [23, 24]. However, this method includes long-term and high-temperature calcination since the reaction only occurs at the particle's interface; small particle size together with an effective mixture is needed to maximize the contact area and minimize the diffusion path, requiring additional milling process. This methodology usually provides powder with a lack of homogeneity, secondary phases, and large particle size [25, 26]. Due to the disadvantages of solid-state reaction methods, chemical routes have emerged to synthesize ceramic materials, such as hydrothermal [27–29], combustion method [10, 30], and sol–gel [31–33].

The flexibility of the sol–gel route, particularly the Pechini method, allows homogeneous solutions with great particle size and morphology control, making this method very attractive [34–36]. Additionally, the Pechini method allows pure materials to be treated at lower temperatures and time, making this method one of the most widely applied chemical routes to obtain ceramic materials [37, 38].

The production of metallic citrate can characterize Pechini's method, forming a polymeric network through an esterification reaction in which three-dimensional crystals can be achieved after thermal treatment. Some advantages of using the Pechini route are different temperatures and proportions of reagents, low-cost materials, reasonable control of the size and stoichiometry of the products, homogeneous compositions, and high-purity material at low calcination temperature [33, 35, 37].

This article compares preparing calcium pyrovanadates through the solid-state reaction method and the modified Pechini method. Even exploited since 1981, the synthesis of $\text{Ca}_2\text{V}_2\text{O}_7$ via the Pechini method has never been reported [8, 9, 19, 20, 39–44].

The influence of the synthesis route can change material characteristics such as particle morphology, size, crystal-line structure, and optical properties. The powder obtained through the Pechini method was tested in the photocatalytic decolorization process of MB.

Experimental section

This work aimed to compare $\text{Ca}_2\text{V}_2\text{O}_7$ synthesized by different synthesis routes and how the process route influences the final properties of the material and finally apply the best formulation as a photocatalyst in a water treatment containing methylene blue (MB).

For the experiments, two routes to synthesize $\text{Ca}_2\text{V}_2\text{O}_7$ were chosen, and three different temperatures applied (650, 750, and 850 °C) were used, for which the solid-state reaction method so far described in the literature [21] and the sol–gel method developed by Maggio Pechini with modifications well known for the synthesis of ceramic materials, but never applied for the synthesis of $\text{Ca}_2\text{V}_2\text{O}_7$ specifically. All sample references and synthesis methods are reported in Table 1. The graphs presented in this work were made via Origin 2020b (Academic version).

Solid-state reaction

The $\text{Ca}_2\text{V}_2\text{O}_7$ powder was prepared using the solid-state reaction method based on calcium carbonate CaCO_3 (Êxodo Científica—98%) and vanadium pentoxide V_2O_5 (Dinâmica—98%), all from Brazil. Stoichiometric amounts in molar ratio 2:1 of CaCO_3 and V_2O_5 were mixed for 15 min at 300 rpm in a planetary ball mill using zirconia balls as grinding agents in ethanol (99%). The mixed powders were dried under an infrared lamp for 12 h and then calcined in an electric muffle at 650, 750, and 850 °C for 2 h in an air atmosphere with a heating rate of 10 °C/min.

Modified pechini method

The modified Pechini method was employed to prepare the calcium pyrovanadate using a molar composition of 1:1.5:5 (metal/citric acid/ethylene glycol). First, an appropriate amount of citric acid (Dinâmica—99.5%) was dissolved in deionized water at 60 °C under magnetic stirring, highlighting this step as a modification of the original Pechini

Table 1 Powder formulations, synthesis methods, and samples references

Calcination temperature	Synthesis method	Sample references
650 °C	Solid-state reaction	F650
	Modified Pechini	Q650
750 °C	Solid-state reaction	F750
	Modified Pechini	Q750
850 °C	Solid-state reaction	F850
	Modified Pechini	Q850

methodology [34], followed by the addition of ammonium metavanadate NH_4VO_3 (Dinâmica—98%). Furthermore, calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Êxodo Científica—99%) was added to the solution, and ethylene glycol (Vetec—99.5%) was added around 90 °C. All reagents were purchased from Brazil. The solution was kept under continuous stirring at this temperature until the jellification process was achieved. Finally, after drying the gel at 150 °C, the resulting powder was calcined in an electric muffle at 400 °C for 4 h to eliminate part of the organic matter, followed by another calcination at 650, 750, or 850 °C for 2 h at air atmosphere using a heating rate of 10 °C/min to obtain the final product.

Characterizations and measurements

Thermogravimetric analysis (TGA) was performed in the oxide mixtures and the polymer precursor after dehydration at 400 °C for solid-state and modified Pechini, respectively. It was carried on in a Jupiter NETZSCH STA 449 C equipment, using synthetic air atmosphere, heating from 25 to 1400 °C, and a heating rate of 10 °C/min. Alumina crucibles and a gas flow of 50 ml min⁻¹ were used. The crystalline phases were characterized by X-ray diffraction (XRD) using X-ray Diffractometer XRD-7000 equipment (Shimadzu®), with Cu-k α radiation ($\lambda = 0.15406$ Å), monochromatic X-Ray source, operated at 40 kV and 30 mA. The analysis was performed with a 2 θ range of 10–70° and a scan rate of 0.6° min⁻¹. After synthesis, to reduce the grain size, the powders were milled in the planetary ball mill (FRITSCH PULVERISETTE 5) using a nylon jar with zirconia-yttrium balls (NETZSCH 3 mm) in deionized water at a rotation speed of 300 rpm for 15 min. The suspension was dried under infrared lamps (SCT E27R125 IR220/250) for 24 h. The particle size distribution (PSD) of the $\text{Ca}_2\text{V}_2\text{O}_7$ powder before and after milling was determined using SALD-2201 equipment (Shimadzu®) in water at room temperature. Previously, the powder was dispersed in a 2% sodium hexametaphosphate aqueous solution in a beaker under ultrasound for 15 min. The surface area for the samples synthesized at 850 °C (for solid-state reaction and Pechini method) was

measured using the Brunauer–Emmett–Teller method in an ASAP 2000 surface area analyzer (Micromeritics Instrument Corp.).

Microstructure observations were made using a JEOL scanning electron microscope (SEM) operated at 15 kV and 10 A with Au-sputtered samples.

The optical analysis and band gap estimation were carried out with diffuse reflectance spectroscopy in the UV–Vis region carried out in UV–Vis Varian Cary 50 Conc with the Barreline, Harrick Scientific, accessory. The diffuse reflectance spectra were converted to absorption spectra based on the Kubelka–Munk theory with a D65 light source and an observer angle of 10°. The spectra were collected in the 200 to 800 nm range at room temperature using BaSO_4 as a reference to the baseline. Diffuse reflection data were converted using the Kubelka–Munk transformation implemented in the spectrometer's software. Band gaps were extracted from Tauc plots of the Kubelka–Munk transformed reflection data based on Ref. [45, 46].

The photocatalytic activity of $\text{Ca}_2\text{V}_2\text{O}_7$ was synthesized via modified Pechini at 850 °C by the photo-bleaching of MB solution [i.e., $(\text{CH}_3)_2\text{N}(\text{C}_6\text{H}_3)\text{NS}^+(\text{C}_6\text{H}_3)\text{N}(\text{CH}_3)_2\text{Cl}^-$] under ultraviolet irradiation (UV-C lamp OSRAM, 36W, dominant wavelength $\lambda = 254$ nm). The experiment was carried out in a homemade reactor, as shown in Fig. S.1 in the supplementary data, consisting of a black plastic box containing a cylindrical glass with 500 ml of MB solution (10 mg L⁻¹) in the presence of 10 μL of H_2O_2 (30%) and 1 g of $\text{Ca}_2\text{V}_2\text{O}_7$ in the form of dispersed powder; the system was maintained under constant stirring, with the surface of the liquid 5 cm far from the lamp, and the pH of the solution was kept as natural around 6.0.

Results and discussion

To compare the difference between the solid-state reaction method and Pechini and how it influences the final properties of the material, an investigation was conducted for the microstructural and optical properties. In the end, the

Fig. 1 The DTA/TG curves of the thermal decomposition of the $\text{Ca}_2\text{V}_2\text{O}_7$ precursor synthesized by **a** the solid-state reaction method and **b** the modified Pechini method

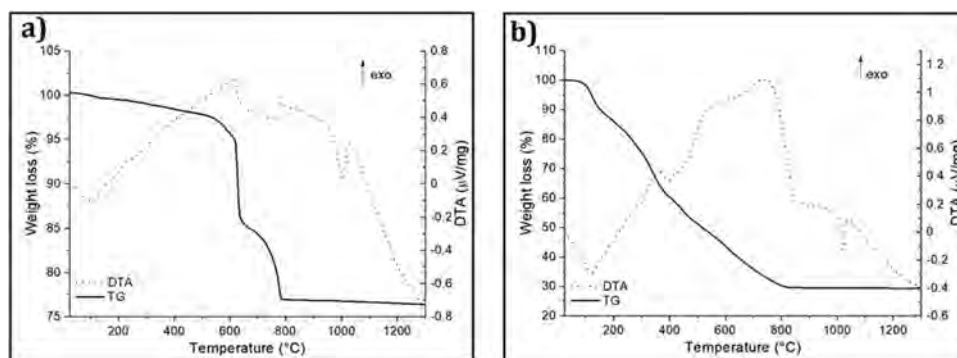
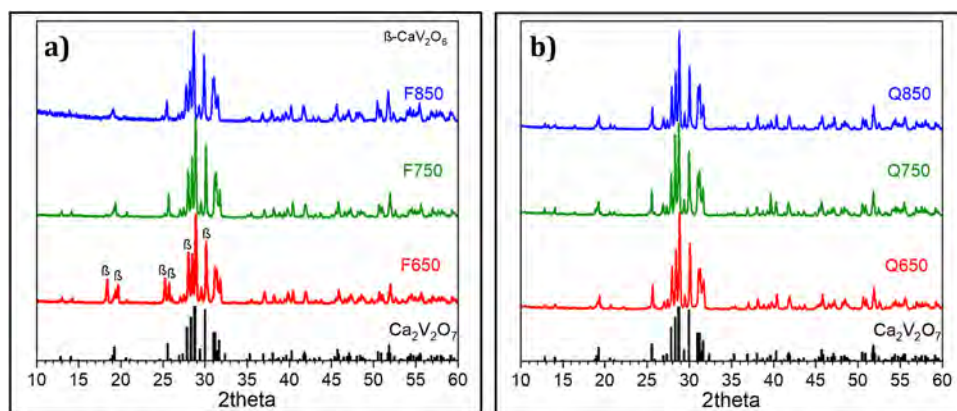


Fig. 2 XRD pattern of calcium pyrovanadate after calcining at different temperatures applying **a** the solid-state reaction and **b** Pechini method



best-synthesized powder was tested as a photocatalyst in a photo-induction test to decompose MB.

The thermogravimetric analysis of precursors provided information about the thermal behavior of this material.

Figure 1 shows the TG and DTA results for precursors obtained by solid-state reaction and modified Pechini method.

In the solid-state reaction precursor, there are well-defined stages of weight loss, suggesting the decomposition

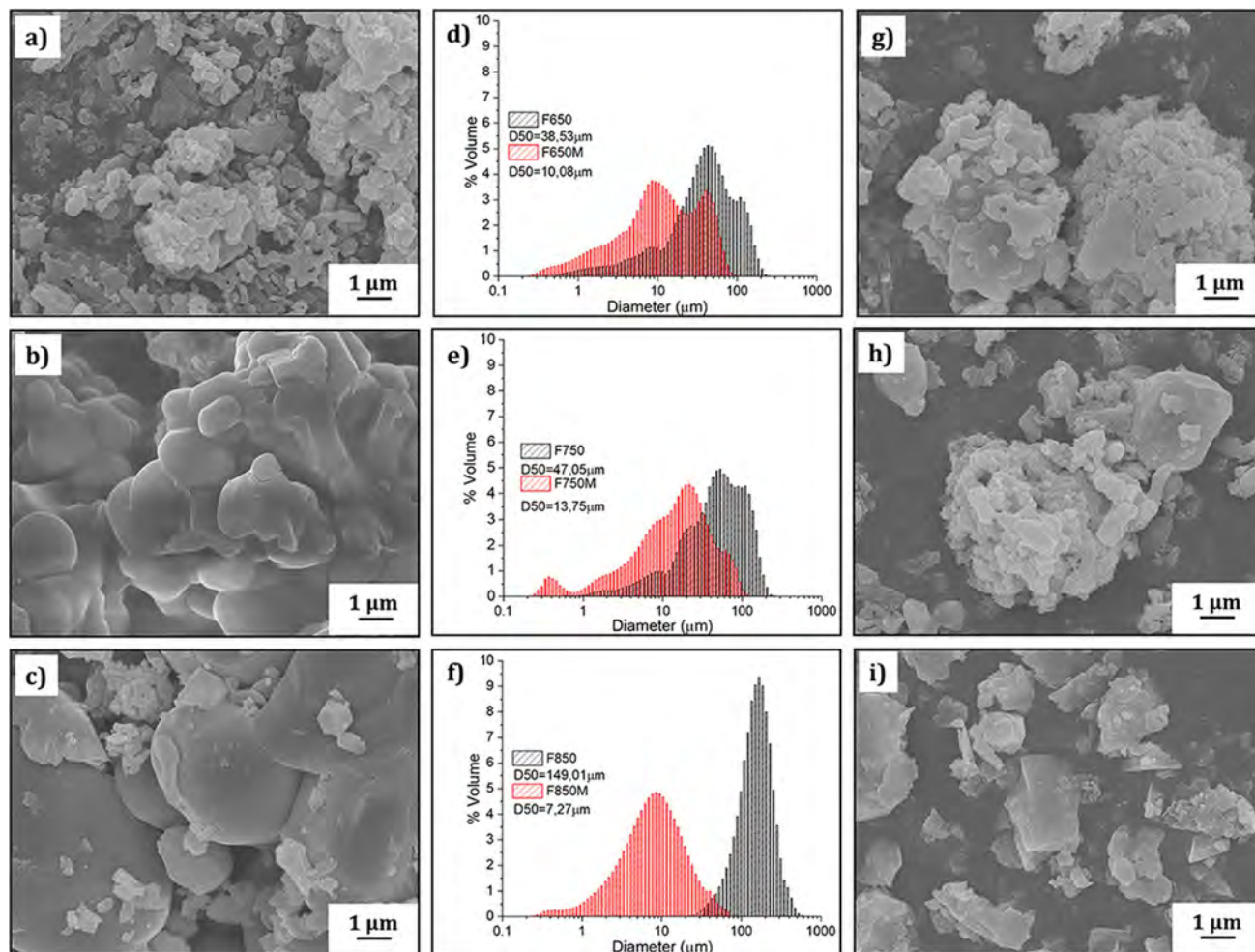


Fig. 3 SEM images for $\text{Ca}_2\text{V}_2\text{O}_7$ synthesized by the solid-state reaction method before milling (**a**, **b**, **c**), after milling (**g**, **h**, **i**), and PSD distribution (**d**, **e**, **f**)

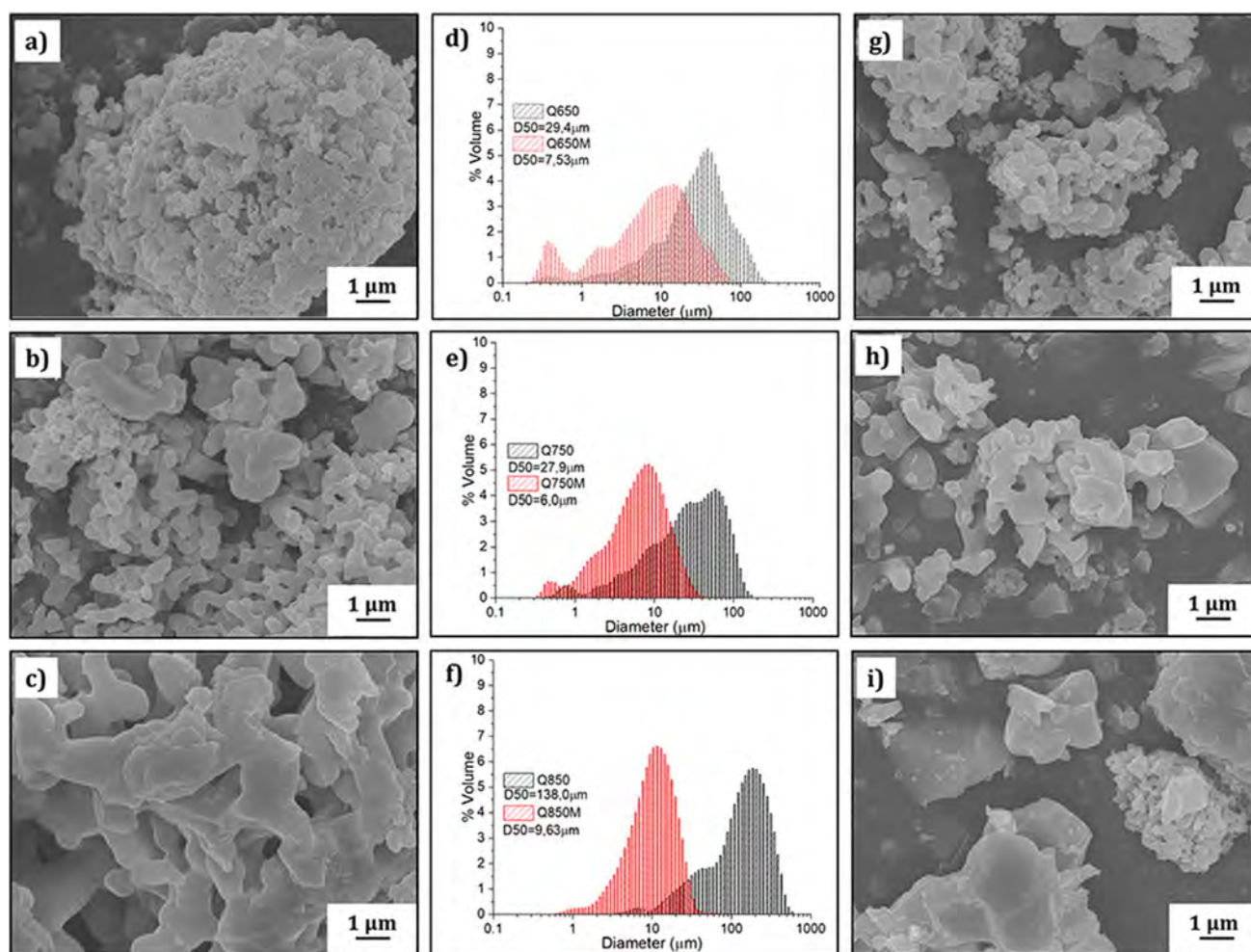


Fig. 4 PSD distribution and SEM images for $\text{Ca}_2\text{V}_2\text{O}_7$ synthesized by the modified Pechini method before milling (a, b, c) and after milling (d, e, f)

temperature of CaCO_3 . An exothermic event appears between 600 and 800 °C that can be associated with the formation of crystalline structure, and another exothermic event shows a melting temperature at almost 1000 °C. This phenomenon has already been previously reported by Ref. [47] in the synthesis of calcium pyrovanadates by the solid-state reaction method. The same events appear for the modified Pechini precursors, but the weight loss for this route is more expressive because of the characteristics of this methodology (humidity and organic compounds).

The exothermic event associated with the melting temperature also appears in the same temperature range in the

solid-state reaction method, but in a range more extensive than the modified Pechini, due to the presence of intermediate phases. The solid-state reaction involves heating the particles that react to form the required product. Reactions such as the solid-state method produce secondary phases since the reaction can only occur at the interface of the two solids. Once the surface layer has reacted, the reaction continues as the reactants diffuse from the bulk to the interface. This way, intermediate phases are created during the reaction and consumed by the major phase $\text{Ca}_2\text{V}_2\text{O}_7$ [48].

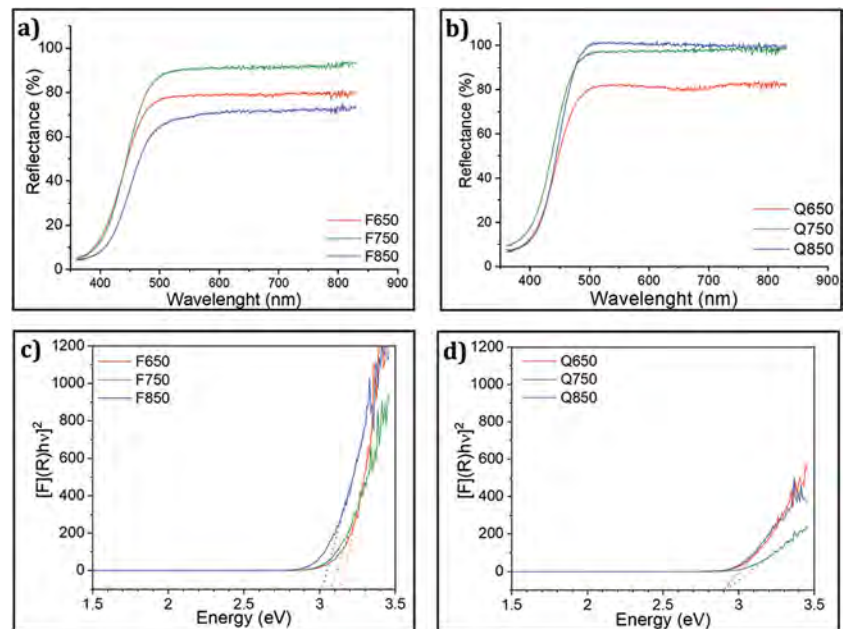
The crystalline phases of the synthesized powders were identified by XRD (Fig. 2). Regarding the solid-state reaction method (Fig. 2a), the primary phase is $\text{Ca}_2\text{V}_2\text{O}_7$ (JCPDS 00–038–0284), with a minor secondary phase, identified as CaV_2O_6 (JCPDS 01–073–0186), being an intermediary product on the obtention of $\text{Ca}_2\text{V}_2\text{O}_7$.

Previous work reported the same intermediary phases for the solid-state synthesis of $\text{Ca}_2\text{V}_2\text{O}_7$ [20]. The increase in the reaction temperature results in the reduction or even

Table 2 Surface area and particle diameter via BET

	BET surface area (m^2/g)	Diameter (nm)
F850	0.0424	4224
Q850	0.2862	626

Fig. 5 Diffuse reflectance spectra for $\text{Ca}_2\text{V}_2\text{O}_7$ synthesized by the solid-state reaction (a) and Pechini method (b); Tauc plots for F650, F750, and F850 (c) and Q650, Q750, and Q850 (d)



elimination of the residual secondary phase. On the other hand, the melting temperature is nearly 1000 °C, limiting the synthesis temperature. Furthermore, the methodology developed by Pechini produced a monophasic material, which is identified as $\text{Ca}_2\text{V}_2\text{O}_7$ (JCPDS 00–038–0284), regardless of the calcination temperature, as expected for this methodology, since it promotes a lower energy crystallization process.

The particle size distribution (PSD) curves for synthesized materials before and after milling via the solid-state reaction method are shown in Fig. 3. The results are presented for materials produced at three different temperatures. The size and morphology are illustrated by scanning electron microscopy images that reveal the presence of agglomerates for all materials.

The milling process results in a reduction of average grain size and produces a change in the shape of the distribution curve. Before the milling process, the average grain size of the materials was 38.3, 47.1, and 140.8 μm for calcination temperatures of 650, 750, and 850 °C, respectively. The SEM images show that with the increase in the calcination temperature, the sintering process is more evident, offering a coalescence between the particles forming a dense, nonporous network, explaining the significant increase in the average size of the

material. The average grain sizes after milling were 10.0, 13.8, and 7.3 μm for 650, 750, and 850 °C, respectively. The significant reduction in particle size with milling indicates that the powder-synthesized materials are made of fragile agglomerates that can easily be fragmented. The different morphologies in the SEM images can be associated with the second phase shown in the XRD pattern.

The particle size distribution (PSD) curves for synthesized materials by the modified Pechini method before and after milling are shown in Fig. 4. The results are presented for materials produced at three different temperatures, as applied for the solid-state reaction. The size and particle morphology illustrated by scanning electron microscopy images before milling reveal that the grain size average is 29.4, 27.9, and 138.3 μm .

Subsequently, this is reduced to 7.5, 6.0, and 9.6 μm with a bimodal distribution after the milling process for the material synthesized by the Pechini method at 650, 750, and 850 °C, respectively.

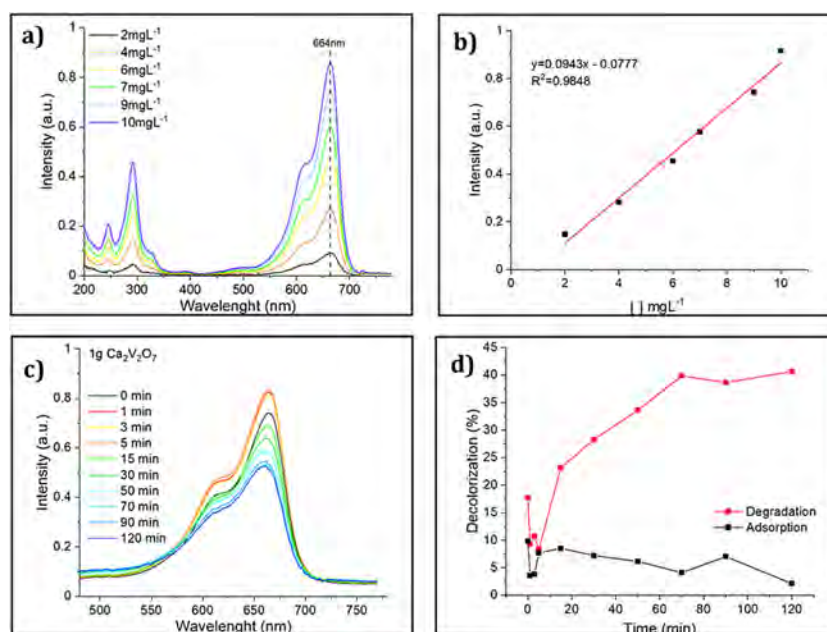
The $\text{Ca}_2\text{V}_2\text{O}_7$ powder produced by modified Pechini is made of small particles in fragile agglomerates; the same morphology was observed at all temperatures, with smaller particle sizes and more homogeneous morphology if compared to the material from the solid-state reaction method. The relationship between calcination temperature and particle size is not maintained. At higher temperatures, even with the sintering process, porosity is presented.

The BET analysis was performed in the powder synthesized at 850 °C for both methods. The particle size was calculated according to Beaugregard [49], where the density applied for the calculation was 3.35 g/cm³ [50]. Table 2 brings the surface area obtained via BET methodology together with the calculated particle diameter.

Table 3 Band gap of synthesized $\text{Ca}_2\text{V}_2\text{O}_7$ according to synthesis route and calcination temperature

	$n = 2$
F650	3.15
F750	3.08
F850	3.03
Q650	2.91
Q750	2.92
Q850	2.90

Fig. 6 Photocatalytic activity of $\text{Ca}_2\text{V}_2\text{O}_7$: **a** different concentrations of MB solution, **b** MB calibration curve, **c** MB decolorization under ultraviolet irradiation with 1 g of catalyst, and **d** MB decolorization and adsorption curve of MB in $\text{Ca}_2\text{V}_2\text{O}_7$



The calculated diameter shows that the Pechini provides particles almost 7 times smaller than the ones from the solid-state reaction method, already expected from the Pechini route, since this methodology is known for offering high pure materials together with small particle size and high surface area [25, 26, 32].

The diffuse reflectance spectra of the $\text{Ca}_2\text{V}_2\text{O}_7$ powders calcinated at different temperatures are shown in Fig. 5, where both the synthesized via solid-state reaction (Fig. 5a) and Pechini method (Fig. 5b) present a great absorption of UV light in regions under 500 nm.

A visible semiconductor behavior can be observed from optical assays. The analysis of Kubelka–Munk plots shows a quadratic dependence on reflectivity near the band gap, indicating a direct band gap typical of most low-symmetry vanadates [51]. The estimated optical band gaps determined from the Tauc plot are shown in Table 3.

As can be seen, the samples show an absorption of around 460 nm. The band gap is 3.00 ± 0.09 eV, similar to that obtained in previous works [8, 20]; using the modified Pechini method, it is slightly smaller than those obtained via solid-state reaction, probably associated with a higher purity material once the band gap for $\text{Ca}_2\text{V}_2\text{O}_7$ obtained in Project TM [50] via DFT calculation is 2.96 eV.

$\text{Ca}_2\text{V}_2\text{O}_7$ as a photocatalyst for degradation of MB dye solution

The photocatalytic degradation of MB dye solution by $\text{Ca}_2\text{V}_2\text{O}_7$ (Q850) obtained via the Pechini method under

ultraviolet irradiation is shown in Fig. 6. In the absorption spectra (Fig. 6c), it can be seen that the intensity of MB decreased with increasing irradiation exposure, indicating that the solution had been decolorized.

With 120 min of radiation exposure, the MB solution deteriorated by more than 40%. Using a 500-W (Xenon bulb—visible light source) lamp and a similar material (CaV_2O_6), the authors were able to decolorize the sample to 80% in 120 min [52]. It is crucial to note that the lamp used for the tests performed in our study is almost 14 times less potent than the one used in Yu et al. [52], is also less expensive, and requires no additional cooling system.

Conclusions

This paper has shown the influence of different synthesis methodologies on the properties of $\text{Ca}_2\text{V}_2\text{O}_7$ by comparing the solid-state reaction and chemical route developed by Pechini. Both routes could successfully synthesize $\text{Ca}_2\text{V}_2\text{O}_7$, and their respective materials showed a melting temperature close to 1000 °C and a medium particle size after the milling process of around 4 μm .

The solid-state reaction shows an intermediary phase when synthesized at a lower temperature (650 and 750 °C), reaching a higher purity at 850 °C, presenting material which the main phase identified as $\text{Ca}_2\text{V}_2\text{O}_7$, with an average band gap of around 3.09 ± 0.05 eV; on the other hand, the modified Pechini route shows the monophasic material in all calcination temperatures applied as well as smaller

particle size distribution, more homogeneous morphology presenting high porosity, and a slightly smaller band gap of 2.91 ± 0.008 eV.

The difference in the band gap could be associated with the purity of the powder since the solid-state reaction method presented a polyphase material between 650 and 750 °C; however, in 850 °C in both synthesis routes, the band gap is the same, evidencing that the purity of the material influences. Sharma and his research group synthesized $\text{Ca}_2\text{V}_2\text{O}_7$ through modified chemical precipitation and annealing and obtained a band gap of 2.67 eV [8]. The band gap near 3 eV is very typical of vanadates [8, 11, 53], being a consequence of the fact that the top of the valence band and the bottom of the conduction band are dominated by O 2p and V 3d orbitals, with little contribution of Ca state near Fermi level [8, 11, 54–56], being useful for UV-induced photocatalytic degradation of organic pollutants [48, 57, 58]. Incident photons with higher energy than the band gap energy are also absorbed, and, as a fact, electrons jump from the valence band to the conduction band. Subsequently, pairs of electron–hole particles appear [48]. These pairs of particles exhibit oxidative and reductive properties, promoting redox reactions in photocatalytic experiments [48].

According to this work, the $\text{Ca}_2\text{V}_2\text{O}_7$ synthesized by the Pechini method shows to be the most suitable material for the photocatalytic test. Once this method provides a higher purity material, together with a bigger surface area and a band gap closer to the theoretical obtained via DFT calculations [50].

This material is promising for application in advanced oxidation processes (AOP) for wastewater treatment since the band gap is approximately 3 eV, it has a very porous structure, and it was able to photodegrade MB in more than 40% in 120 min.

Despite limitations due to the radiation source and the handmade reactor, we believe this work provides a significant step toward the choice of synthesis route to obtain $\text{Ca}_2\text{V}_2\text{O}_7$ for application in the photocatalyst field.

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Data Availability The data is available if requested via email.

Declarations

Conflict of interest The authors declare no competing interests.

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Sustainable silico-aluminous refractory wastes as an alternative raw material for hydraulic binder for foundry industry

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Calcium aluminate
Recycling

ABSTRACT

The foundry industry is responsible for consuming large quantities of lining materials and generating significant amounts of waste. Silico-aluminous linings are used in the production of cast iron due to their compatibility with molten metal and slag. However, after use, these materials are typically disposed of in industrial landfills, creating an environmental liability. This study demonstrated a feasible alternative approach to repurpose silico-aluminous refractory wastes from induction furnaces and casting ladles from the foundry industry to develop new materials for refractory hydraulic binders for lining (refractory patch). The wastes were characterized using X-ray Diffraction, X-ray Fluorescence Spectrometry, Thermal Analysis, Scanning Electron Microscopy, and particle size distribution. The behavior of the lining wastes was found to be compatible with the proposed application, despite the expected contamination. There is potential for cost savings of at least 25 % and promoting a culture of recycling.

1. Introduction

The Brazilian production of cast materials, in 2021, was over 2,706 thousand tons, with 91 % of this value related to the ferrous industry. Despite the impact of the economic crisis generated by the pandemic, the sector showed growth during 2021 (ABIFA - Brazilian Foundry Association, 2022). The increase in the production of castings also results in an increase in the volume of waste generated, which can negatively reflect on the performance of the sector's environmental indicators (Xiang et al., 2019). According to the Global Reporting Initiative, there are various environmental indicators (Globalreporting.org, 2020; Hourneaux Junior and Hrdlicka, 2011), such as indicators related to the use and recycling of materials, emissions, effluents, and waste. To minimize the negative impact of these indicators, several actions can be taken, such as reducing the consumption of natural raw materials, reducing the generation and disposal of waste, and using by-products to replace natural raw materials.

Silico-aluminous refractory materials are widely used in the foundry industry. The increase in the lifetime of the refractory material can be

associated with a reduction in the consumption of raw materials, in addition to minimizing the need to dispose of the refractory used (Krause, 2017; Muñoz et al., 2020). Thus, the sector invests in the development of projects, in controlling the composition of refractories, and in the adequate choice of materials for each condition (Hourneaux Junior and Hrdlicka, 2011). However, there are no refractories that have the properties to work under the action of many aggressive conditions without any damage. The result is the generation of a significant volume of refractory waste (Weinberg et al., 2016).

For this reason, a large part of the refractory waste is discarded, and waste recycling generally has not been used, mainly due to the abundance of virgin raw materials, the low cost of producing refractory materials, and the ease of disposal of materials, which most are classified as inert waste (Hanagiri et al., 2008; Kazemi and Golestani-Fard, 2007; Smith et al., 1999). In general, recycling is difficult since the waste results from the combination of refractory mixtures that are difficult to separate by type and mainly due to the contamination present during the material use. This contamination causes difficulty for the refractory waste to meet the quality standards required to be used as refractory raw

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materials (Horckmans et al., 2019). Sá et al. (2007), Gumpenberger et al. (2008), Connemann et al. (2016), Baryshnikov et al. (2016), Günther et al. (2016), Noll et al. (2018), presented several developed systems, many of them patented, for pre-classification by type of refractory waste, as a way of identifying materials, enabling the recycling of waste.

Luza et al. (2022) demonstrated the viability of recycling MgO waste refractories in refractory masses. Liu et al. (2023) investigated two lightweight periclase-magnesium aluminate spinel refractories and compared them with commercial dense refractories. Ikram-Ul-Haq et al. (2012) and Bradley (2016) highlight the importance of controlling the iron content present in the waste, which comes from the inherent contamination in the ferrous casting process. High-temperature interactions of recycled refractory substrates with molten iron showed that

chemical interactions in $\text{Al}_2\text{O}_3\text{-C/Fe}$ system resulted in interracial cracks, degradation in the structural integrity of refractory substrates, modifications to contact angles, and carbon pick-up when spent refractories were remixed with virgin refractory constituents. The quality of recycled refractory was significantly lower than that of virgin refractory. Therefore, in this study, waste with and without partial removal of Fe iron was investigated. López-Perales et al. (2021) developed a sustainable conventional refractory castable with improved properties incorporating blast furnace slag at 10 wt% containing 0.94 wt % of the Fe_2O_3 . El Haddar et al. (2019) developed refractory bricks based on raw halloysite mixed with silico-aluminous mineral aggregates and improved with the addition of recycled alumina.

Aiming to reuse waste generated by the foundry industry, siliceous-

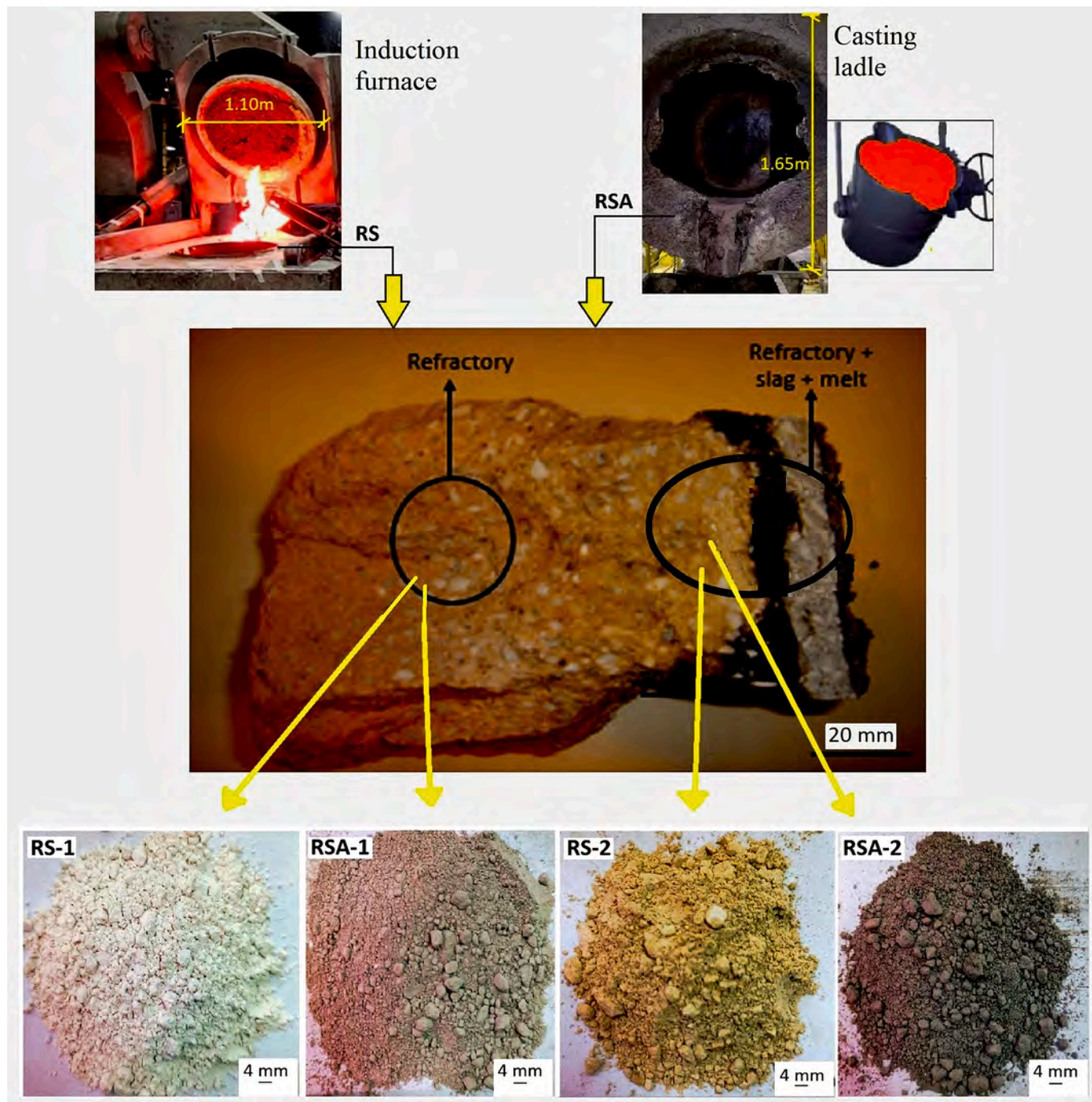


Fig. 1. Representative image of a refractory fragment removed from the furnace and casting ladle.

refractory waste from induction furnaces, and silico-aluminous refractory waste from casting ladles were characterized to assess their potential for use in obtaining refractory patch mass. To accomplish this, the siliceous-refractory waste and silico-aluminous refractory waste, as well as the refractory patch mass after the incorporation of the wastes and a commercial refractory patch mass, were subjected to characterization using various techniques.

2. Materials and methods

The materials used were the siliceous-refractory waste (RS) and the silico-aluminous refractory waste (RSA) as raw material for obtaining hydraulically silico-aluminous refractory set mass, industrially known as *refractory patch mass*. As a reference material, a commercial refractory patch mass was used, which was referred to as MC. The refractory patch mass of control (MP) was determined, and the refractory patch masses with the wastes were defined from the combination of silica (SiO_2) and silico-aluminous ($\text{SiO}_2\text{-Al}_2\text{O}_3$) refractories wastes in partial or total replacement (25, 75 and 100 wt%) of the conventionally used silica sand.

2.1. Siliceous-refractory waste, silico-aluminous refractory waste, and MC materials

The RS waste comes from the induction furnaces and the RSA waste comes from the casting ladles used in the melting of cast iron. Approximately 10 kg of RS and RSA wastes were provided by a partner global foundry company specialized in developing and manufacturing highly engineered structural cast iron components, located in the state of Santa Catarina, Brazil. The samples were taken shortly after they were removed from the induction furnace and casting ladle (Supplementary Fig. 1). The original lining which gave rise to the RS wastes has a lifetime of around 15 weeks (4-ton fusers), 10 weeks (8-ton fusers) and 6 weeks (12-ton fusers), and RSA wastes 4 months (cast iron pot), 8 weeks (for repairs) and a full replacement every two years. The wastes consisted of large fragments of material composed mainly of refractory (25 %), containing a dark, whitish surface layer, which was formed by the interaction between the refractory and the melt, composed of metal and slag formed in the casting process (Fig. 1).

The received material was processed to obtain two different types of samples. In the first case, the separation of the surface fraction containing metal and slag was performed, resulting in a material called R1. The separation was carried out through visual analysis and manual fragmentation. In the second case, the refractory was used as received, without removing the transition zone, resulting in the material called R2. The procedure was performed for the siliceous-refractory (RS), generating the RS-1 and RS-2 fractions, and for the silico-aluminous refractory (RSA), generating the RS-1, RS-2, RSA-1, and RSA-2. The materials thus divided were ground using a pan crusher with rings until 100 % of the particles did not exceed a maximum particle size of 7 mm (range of 2.36–6.70 mm). The waste had larger particles of agglomerated material after drying at 105 °C. Therefore, it was sieved through a 1.18 mm sieve. Only the fraction smaller than 1.18 mm was used in the study.

The RS and RSA wastes, the reference refractory patch mass, and the other raw materials (silica sand, chamotte, and aluminous cement), were characterized in terms of their chemical composition, mineralogical composition, and thermal behavior. X-ray diffraction was performed using Shimadzu XRD-6000 equipment with a copper target and a scanning speed of 2°/min. The material was analyzed in powder form within the range of 5–90 degrees, with a total of 5 random samples for each waste, representing a total of 10 kg (10 g representative samples). Chemical analysis was conducted using an X-ray spectrometer by EDS Shimadzu model EDX-720, with a maximum particle size passing #200 (75 μm). Thermogravimetric analysis and thermal analysis were carried out using NETZSCH equipment with a heating rate of 10°/min, in the

temperature range of 25–1400 °C in an oxidizing atmosphere, with maximum particle size of 75 μm . SEM images were acquired using field emission scanning electron microscopy (FE-SEM) on a JEOL instrument model JSM 6701F.

The particle size distribution of the ground materials was determined using sieve meshes ranging from 2.36 to 6.7 mm, following NBR 6946 (ABNT, 2015a).

The MC is used as a refractory lining, composed of silica sand, chamottes C-85, aluminous cement (60 % of Al_2O_3 and 32 % of CaO), and water. It has a cold crushing strength ≥ 10 MPa and a bulk density ≥ 2.2 g/cm³ after treatment at 750 °C. The RS and RSA wastes and the MC were characterized through leaching and solubilization tests according to the NBR 10004 waste classification standard (ABNT, 2004).

2.2. Raw materials

The commercial raw materials used were silica sand 58/68 (92.02 % of silicon oxide with impurities present in low levels, the bulk density obtained was 1.48 g/cm³, particle size between 0.150 and 0.106 mm, and the rest of the particles distributed in meshes from 0.6 to 0.3 mm, and the fine particles content was around 1.26 %), chamotte C-85 (10.49 % of silicon oxide, 81.70 % of Al_2O_3 , the coarse material showed a concentration of medium chamotte particles in the 1.18 mm mesh, the fine chamotte showed a concentration of particles between the 0.6 mm and 0.3 mm), and aluminous cement (68.31 % of Al_2O_3 , 27.89 % of CaO , presented a concentration of particles in the 1.18 to 0.300 mm mesh). The siliceous-refractory waste from induction furnaces (RS), and the silico-aluminous refractory waste from casting ladles compost almost 60 % of Al_2O_3 (RSA), and water.

2.3. Experimental design

To determine the mixtures, the Design of Experiments (DOE) statistical experimental model was used. The wastes were incorporated in partial and total replacement, wt.%, of silica sand 58/68 of the MP (control refractory patch mass) mixture. Table 1 shows the composition of the mixtures.

2.4. Preparation of the mixtures

The mixtures were prepared according to NBR-6368 (ABNT, 2011), obtaining the ideal workability. To prepare the mixtures, firstly, a dry mixture of silica sand 58/68, chamotte C-85, and aluminous cement was carried out inside the mixer for one minute, then water was mixed until the workability of plastic refractories by measuring plastic deformation. The water content added was the content necessary to reach the desired workability of the material, which varied between 6 wt% ± 1 .

Table 1
Composition of the mixtures.

Mixtures	Raw material (wt.%)						
	S	C-85	CAC	RS-1	RS-2	RSA-1	RSA-2
MP (control)	25.00	60.00	15.00	–	–	–	–
25 % RS-RSA-1	18.74	60.00	15.00	3.13	–	3.13	–
75 % RS/RSA-1	6.26	60.00	15.00	9.37	–	9.37	–
100 % RS/RSA-1	–	60.00	15.00	12.50	–	12.50	–
25 % RS-RSA-2	18.74	60.00	15.00	–	3.13	–	3.13
75 % RS/RSA-2	6.26	60.00	15.00	–	9.37	–	9.37
100 % RS/RSA-2	–	60.00	15.00	–	12.50	–	12.50

S: Sand; C-85: Chamotte C-85, CAC: aluminous cement, RS-1: siliceous-waste with partial removal of Fe, RS-2: siliceous-waste without partial removal of Fe, RSA-1: silico-aluminous waste with partial removal of Fe, RSA-2: silico-aluminous waste without partial removal of Fe.

For each mixture, the measurement of physical properties (density, water absorption, and open porosity) was carried out according to the NBR 9778 standard (ABNT, 2005).

2.5. Preparation and characterization of test specimens

From the prepared mixtures, approximately 1.5 kg was packaged in a sealed, moisture-proof container. Subsequently, fractions of approximately 225 g were allocated for specimen preparation. These fractions were deagglomerated and placed in a mold to shape specimens with a diameter and height of 50 mm. An impact was applied by allowing a weight of 4.85 N to fall freely from a height of 50 mm (38 percussions on average). The hammer used was a cylindrical steel mold with an internal diameter and height of 50 mm, fixed in a vertical position (Supplementary Fig. 2). The demolding process took place immediately after the sample was formed.

Ambient humidity (before firing) in the formed sample was determined using a moisture analyzer with a capacity of 110 g and a reading of 0.005 g/0.05 % and halogen heating.

After demolding the samples were treated only at 110 °C in a muffle oven, model Jung, for 24 h and then fired at 1400 °C. After firing the samples showed a shrink/expansion. They were cooled naturally to room temperature.

The mechanical resistance analysis of the specimens was conducted on cylindrical specimens measuring a diameter and height of 50 mm through the cold crushing strength test.

The Resistance to Slag Attack test was performed according to the NBR 9641 standard (ABNT, 2015b). For each mixing condition, two samples of specimens fired at 1400 °C were taken. To melt the base alloy of the process, a slag induction furnace located at a partner company was utilized. The synthetic slag used in the test had a basicity of 0.14, classifying it as acidic. The composition of this slag was analyzed via atomic absorption and is reported in Table 2. The crucible of the specimen was filled up to 2/3 of the height and lightly compacted.

The furnace heating rate was set at 5 °C/min. The samples remained in the oven for 4 h, after which the oven was turned off and the samples were allowed to cool to room temperature.

3. Results and discussion

3.1. Characterization of MC, RS, and RSA wastes

The commercial refractory patch mass (MC) consists predominantly of silica and alumina, with a 4.7 % calcium oxide (Table 3). The iron oxide content was around 2.4 %, while the titanium oxide content was 3.1 %.

The siliceous-refractory waste (RS), as expected, exhibits a high SiO₂ content. The efficiency of the separation process, which aimed to isolate the refractory fraction from the region close to the interface between the refractory and the metal, can be demonstrated by the reduced Fe₂O₃ content present in RS-1 compared to RS-2. Additionally, an increase in the alumina content is observed in the RS-2 waste along with the higher iron oxide content. The presence of CaO is likely attributed to the cement used, which may form calcium aluminates that transform into anorthite upon firing. The temperature for the formation of liquid is likely to be the same, and a greater fluxing effect can be attributed to a higher amount of liquid phase. However, in the case of the silica-mullite-anorthite system, an increase in CaO content can lead to a decrease in the amount of liquid formed during initial melting.

The silico-aluminous refractory waste (RSA) exhibits silica and

alumina contents like those found in typical commercial refractory patch masses (MC). Both RSA-1 and RSA-2 share comparable compositions, with the main difference being the higher Fe₂O₃ content in the material that has not undergone removal of the interface between the refractory and the molten metal. Calcium is present in both the silico-aluminous wastes and the refractory patch mass. Calcium oxide is commonly utilized in conventional dense aluminous concretes in proportions exceeding 2.5 wt%. It can exist in the form of calcium hydroxide or calcium carbonate and contributes to enhancing the performance of aluminous concretes by acting as a sintering agent (Lin and Shen, 2013; Luz et al., 2018). Thus, the presence of CaO in silico-aluminous refractory waste does not prevent its utilization as a raw material for producing silica-refractory materials.

Fig. 2a shows the X-ray diffraction pattern of the refractory patch mass MC. The material consists of Corundum (Al₂O₃), ICDD 46-1212, mullite (3Al₂O₃·2SiO₂), ICDD 15-0776 and calcium aluminate (CaO·Al₂O₃), ICDD 45-1374. These crystalline phases are common in aluminous refractories, with mullite being a phase characterized by a low coefficient of thermal expansion, high refractoriness, low thermal conductivity, low chemical reactivity, and high hardness. These characteristics contribute to the superior resistance to thermal shock and high mechanical strength exhibited by refractory materials containing mullite (Krause, 2014; Mourão et al., 2007; Oliveira et al., 2023).

Fig. 2b shows the X-ray diffraction patterns of the RS siliceous refractory. The RS-1 and RS-2 are composed of silica in different polymorphic forms. RS-1 consists of a combination of quartz (ICDD 46-1045) and cristobalite (ICDD 39-1425), while RS-2 is identified to contain quartz, cristobalite, and tridymite (ICDD 42-1401). The presence of these phases is linked to the heating process that the refractory undergoes during its use, involving temperatures reaching approximately 1560 °C (Krause, 2014; Routschka, 2019). The proportion of cristobalite, tridymite, and a minor quantity of quartz may vary over the refractory's lifespan due to the high temperatures and heating-cooling cycles. The tridymite content tends to increase while that of quartz tends to decrease. It is crucial to manage volume variation in many instances, as it can result in internal stresses and the formation of defects in the form of cracks and fissures.

Fig. 2c shows the X-ray diffraction patterns of the silico-aluminous refractory waste (RSA). During its usage, the RSA material was exposed to temperatures of up to 1560 °C. The resulting wastes consist of mullite (3Al₂O₃·2SiO₂) (ICDD 15-0776), Corundum (Al₂O₃) (ICDD 46-1212), and anorthite (Al₂O₃·CaO·2SiO₂) (ICDD 41-1486) as crystalline phases.

When comparing the diffractograms of the commercial refractory patch mass with those of the refractory wastes RSA-1 and RSA-2, it becomes evident that they share similarities in terms of the presence of mullite and alumina phases. Anorthite was present in the waste materials. The diffractogram of the refractory patch mass predominantly showcases alumina, whereas the waste materials exhibit a prevalence of mullite. This phenomenon is expected, given that the waste originates from a heating process that promotes mullite formation.

Fig. 3 depicts the thermal analysis curves of the refractory patch mass, RS refractory waste, and RSA refractory waste. These materials display stable behavior, with a maximum total mass loss <2 wt%. In the case of the refractory patch, the only discernible event takes place at temperatures exceeding 1200 °C, leading to a mass gain of 0.5 %. This increase can be attributed to oxidation effects (Ismael et al., 2007; Ko and Silva, 1997; Mourão et al., 2007).

When comparing the DTA curves of the RS-1 and RS-2 materials, the curve is more pronounced in RS-1. An indication of the transition from α-quartz to β-quartz at 573 °C is evident for both materials, and the endothermic event linked to the material's softening commences at a temperature near 1000 °C (like the refractory patch). This relatively low formation temperature of the liquid phase must be attributed to the presence of fluxes in the material. The temperature at which the liquid phase initiates formation in the refractory patch mass is higher, and this

Table 2
Chemical composition of the slag (wt.%).

SiO ₂	Al ₂ O ₃	MgO	MnO	CaO	FeO
66.76	13.21	4.51	1.21	9.12	5.18

Table 3

Chemical composition of the raw materials (wt.%).

Material	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MnO	CaO	K ₂ O	TiO ₂	Others	loss on ignition (900 °C)
RS-1	91.0	0.4	3.8	–		0.6	–	4.2	0.0
RS-2	82.1	3.2	4.6	0.2	1.0	1.2	0.2	7.2	0.3
RSA-1	25.7	4.1	58.1	0.1	4.2	1.7	2.3	1.7	2.1
RSA-2	25.1	6.5	57.1	0.4	4.2	1.6	2.3	1.8	1.0
MC	22.5	2.4	60.0	0.0	4.7	0.7	3.1	2.9	3.6

aspect must be considered when devising a formulation that incorporates RS waste as a raw material.

When comparing the DTA curves of RSA-1 and RSA-2 wastes, both materials exhibit an endothermic event at a temperature exceeding 1100 °C, which closely resembles the behavior of the refractory patch mass.

The granulometric distribution curve of MC showed small particles (<1 mm), and few medium (around 2 mm), and large particles (>3 mm). This granulometric curve corresponds to an open dispersion of particles and this was suitable for better densification. The granulometric distribution of RS and RSA wastes was like that of MC (Table 4).

Based on the leaching and solubilization tests, RS and RSA wastes, as well as MC, were categorized as non-inert waste under class II.A (Acquapant, 2022a, 2022b, 2021), by the NBR 10004 standard (ABNT, 2004). The wastes are not deemed hazardous and can be safely employed within the foundry industry.

3.2. Results for the mixtures with the wastes RS/RSA-1, RS/RSA-2, and MP

3.2.1. Chemical composition

Table 5 presents the chemical composition of the MP and RS/RSA specimens in fractions 1 and 2, determined on the pure dry mass at 110 °C. MP exhibited Al₂O₃ (62 %) and SiO₂ (28 %), characterizing it as a silico-aluminous refractory hydraulic binder (Mourão et al., 2007). The mixture containing RS/RSA-1 waste showed a lower alumina percentage compared to the MP, alongside higher levels of SiO₂ and CaO. Despite the initial separation of wastes from the metal interface, the Fe₂O₃ content in both RS/RSA-1 and RS/RSA-2 materials was similar. High Fe₂O₃ levels enhance the fluxing effect on silica and alumina. Some studies suggest a low melting point of approximately 1150 °C can be reached in a 1:3 mixture of alumina and silica with 7 % iron oxide under a reducing atmosphere (Cruz, 1987; Krause, 2014; Routschka, 2019). Thus, utilizing siliceous-refractory waste for producing refractory materials for the same purpose should be avoided due to the potential formation of a liquid phase at lower temperatures, resulting in suboptimal performance. However, the results (Table 5) did not exceed 1.92 % iron content. Existing literature and commercial practices (Fe content ≤ 7 %) support the reuse of waste with low iron content. Authors discussing the influence of Fe and Mn oxides on refractory linings used in the melting of ferrous alloys, such as Ko and Silva (1997) along with data presented by Cruz (1987), Refratek (2021), and IBAR (2017), further reinforce the commercial practice by reusing processed waste with Fe content up to 2 %.

The RS/RSA-2 mixtures displayed high alkali content in the material after eliminating the interface between the refractory set mass and the molten metal. These mixtures exhibited slightly higher levels of alumina and lower values of SiO₂ and CaO. This could potentially lead to a minor increase in the quantity of the liquid phase, attributed to the slight rise in alkali contents. The diminished CaO content might yield fewer formed hydrates (only in instances where it is free or forms hydratable phases like aluminates or silicates), further contributing to the overall reduction of the liquid phase and consequently less contraction in the material. The adverse impact of contraction can, in turn, lead to increased porosity, reduced density, and ultimately a decrease in the mechanical strength of the samples.

Calcium oxide is commonly used in conventional dense aluminous concretes, typically at levels exceeding 2.5 % (commercially practiced levels range from 3 to 4.5 %). The RS/RSA-1 mixture exhibited an average CaO content of 8.66 %, while the RS/RSA-2 mixture averaged 7.45 % CaO. The decrease in CaO content in RS/RSA-2 can be attributed to the reduced amount of pure refractory and increased contamination from other components. Both RS/RSA-1 and RS/RSA-2 mixtures demonstrated higher CaO values compared to the MP. This could be viewed as advantageous, as elevated CaO contents can lead to the formation of low melting point compounds, generating a significant volume of liquid phase during heating. This, in turn, may reduce the viscosity of the liquid phase, contributing to increased density and consequently, an augmentation in mechanical strength (depending on the phase to which CaO contributes). However, a substantial amount of liquid phase can potentially decrease the refractoriness of the material, subsequently impacting its resistance (Gerotto et al., 2000; Segadaes, 1997).

3.2.2. Particle size distribution curves, and moisture of the mixtures

The particle diameter size of MP (100 % <1.18 mm) was finer compared to MC (82 % <2.36 mm). When examining the mixtures containing the RS/RSA wastes, it was observed that RS/RSA-1 and RS/RSA-2 contributed to a reduction in the average particle diameter (Supplementary Fig. 3). The presence of the wastes in the mixtures promoted the dispersion of particles, with a higher concentration retained in the 0.6, 0.3, and 0.075 mm mesh sizes. This led to the creation of a particle size distribution curve that displayed a greater dispersion of particle sizes in the fine fraction while reducing particle dispersion in the coarser fraction. This effect could potentially result in a slight increase in packing density as the waste content increases (De Castro and Pandolfelli, 2009; Ortega et al., 1997).

Moisture percentage in the mixtures ranged from about 5 % to 8 %. The MP exhibited the lowest moisture content. When the wastes were introduced to replace conventional silica sand, a minor increase in moisture was observed (Fig. 4), attributed to the slight elevation in fines content within the mixture. The average moisture content among the mixtures was 7 % ± 1.

3.2.3. Density, water absorption, percentage open porosity, and linear dimensional variation

The addition of wastes to replace conventional silica sand did not result in any significant variation in the density of the specimens (p = 0.018), according to Table 6.

The average density value was 2.15 g/cm³ ± 0.07 for the control MP, and similar values were noted for all mixtures. However, higher values were observed for 25 % RS/RSA-1 (2.25 g/cm³ ± 0.06), 75 % RS/RSA-1 (2.30 g/cm³ ± 0.12), and 25 % RS/RSA-2 (2.32 g/cm³ ± 0.01). This increase could be attributed to greater densification of the mixtures due to lower humidity in the specimens, resulting in reduced water absorption after the samples were heated. There was no significant variation in water absorption. The mean water absorption was 13 % ± 1 for the MP mixture, with lower percentages for mixtures containing 25 % RS/RSA-1 (12 % ± 1), 75 % RS/RSA-1 (11 % ± 2), and 25 % RS/RSA-2 (10 % ± 0.01). This decrease might be related to a smaller percentage of open porosity (Duarte, 2011). The percentage of open porosity was higher in specimens containing larger proportions of wastes, specifically

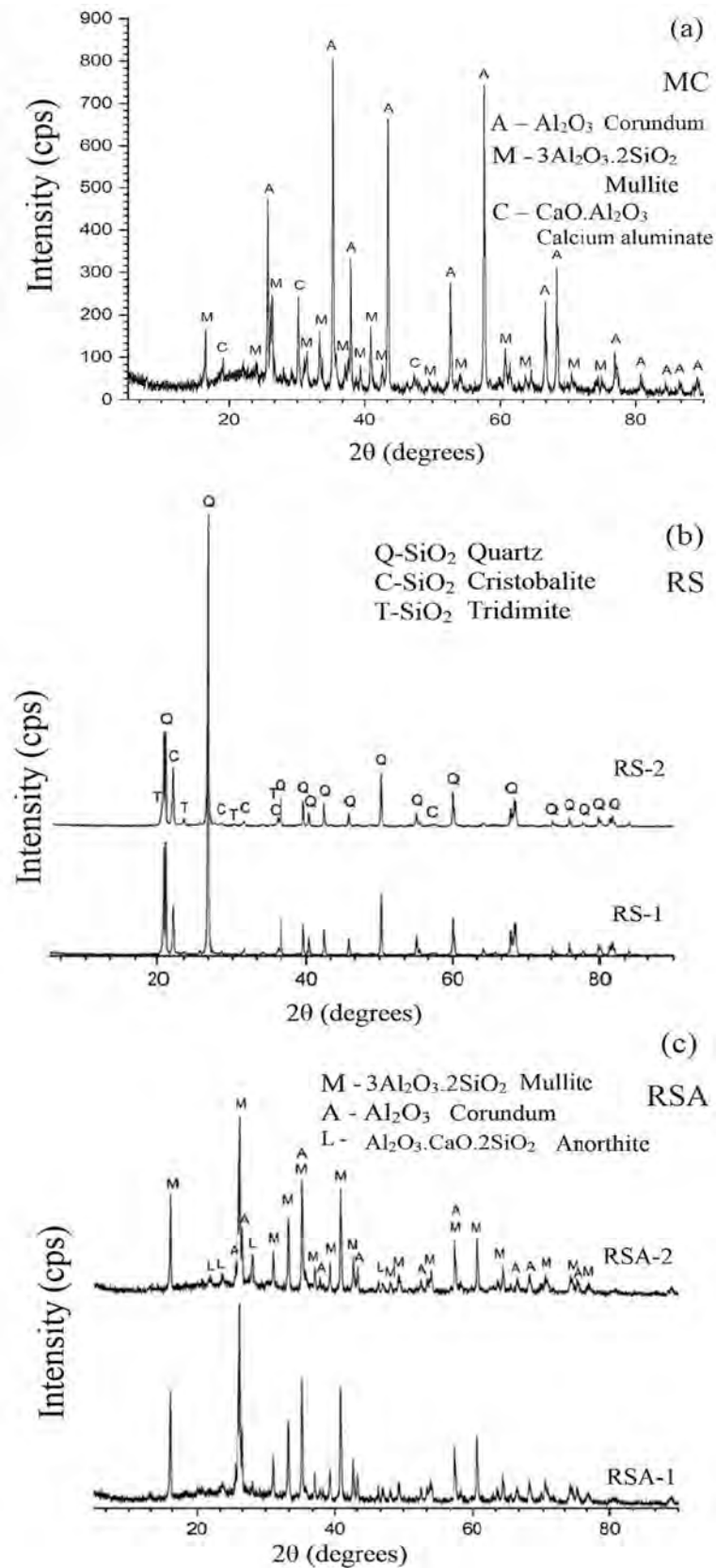


Fig. 2. X-Ray diffractogram of the commercial refractory patch MC (a); RS waste (b); and RSA waste (c).

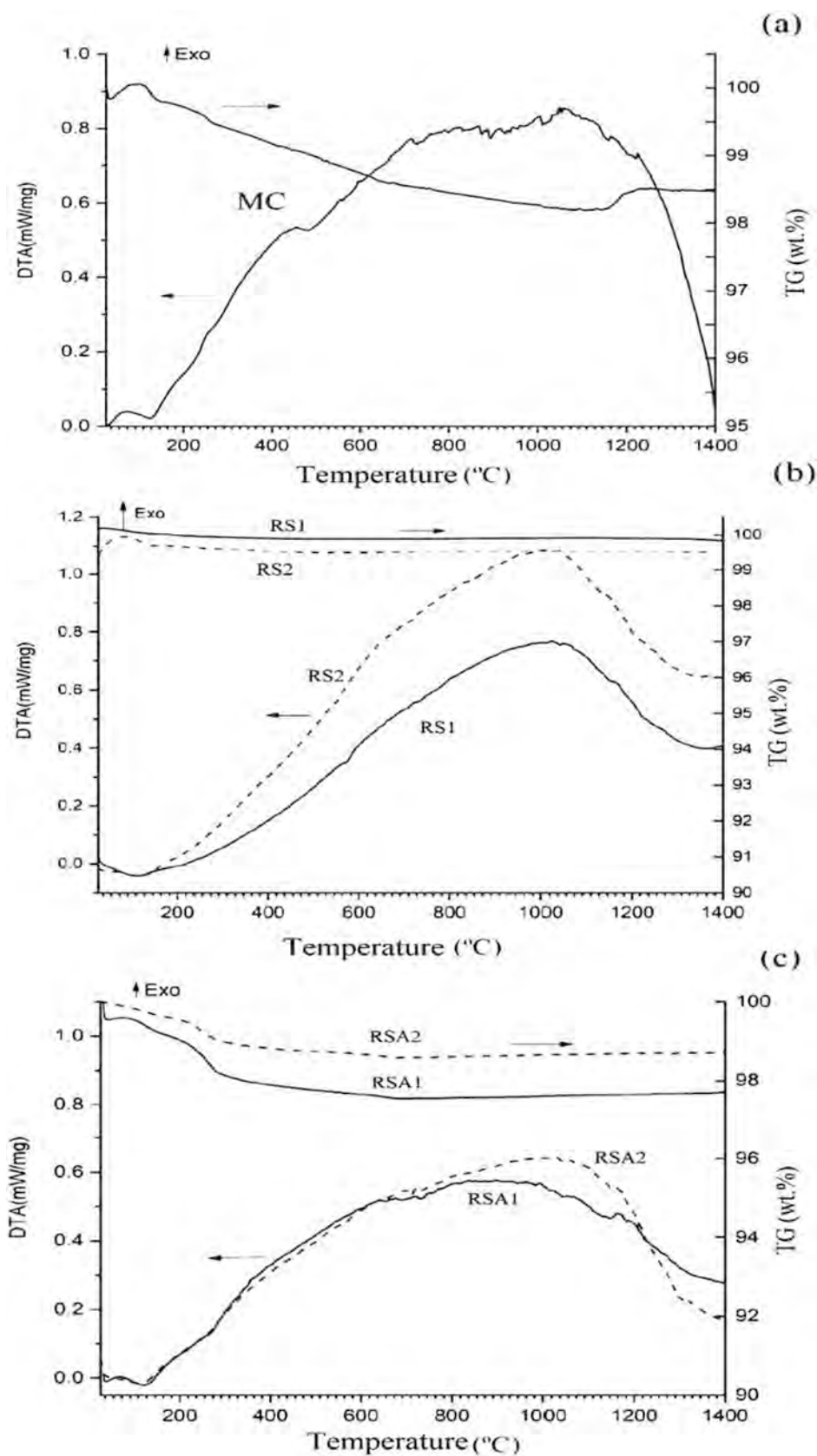


Fig. 3. DTA/TG curves of the refractory patch MC (a); RS waste (b); and RSA waste (c).

Table 4

Particle size distribution of MC, RS, RSA wastes, and conventional sand (wt.% passing).

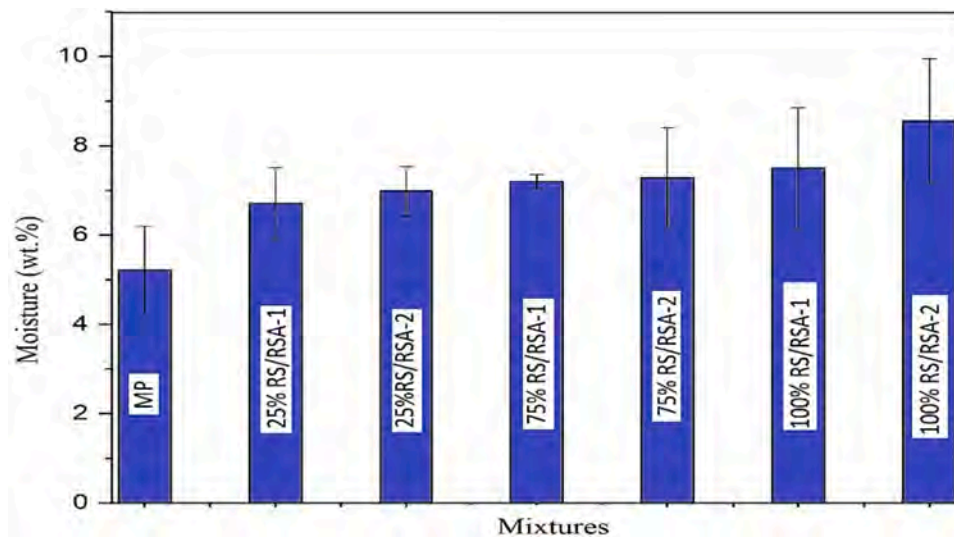
Mesh (mm)	MC commercial	SiO ₂ (RS-1)	SiO ₂ (RS-2)	Al ₂ O ₃ .60 % (RSA-1)	Al ₂ O ₃ .60 % (RSA-2)	Sand
6.70	100.0 %	100.0 %	100.0 %	100.0 %	98.9 %	100.0 %
4.75	99.9 %	100.0 %	96.4 %	96.8 %	96.7 %	99.5 %
3.35	91.9 %	99.7 %	89.2 %	93.1 %	93.2 %	77.8 %
2.36	82.0 %	98.9 %	79.3 %	89.1 %	87.6 %	0.1 %
Mesh plate	0.0 %	0.0 %	0.1 %	0.5 %	2.3 %	0.1 %

*Cumulative values smaller than the mesh size.

Table 5

Chemical composition of the mixtures, obtained by XRF (wt.%).

	MP (control)								
	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	K ₂ O	Zn	MgO	TiO ₂	Other
MP	27.99	1.45	62.00	6.31	0.21	0.036		1.87	0.016
Waste RS/RSA-1									
	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	K ₂ O	Zn	MgO	TiO ₂	Other
25 %	29.03	1.03	57.49	8.64	0.34	–	–	1.28	0.12
75 %	35.49	1.35	52.93	8.56	0.37	0.18	–	0.97	0.08
100 %	36.57	1.43	51.24	8.78	0.46	0.25	–	0.82	0.04
Waste RS/RSA-2									
	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	K ₂ O	Zn	MgO	TiO ₂	Other
25 %	24.24	1.03	59.86	7.65	0.24	0.53	–	1.40	0.05
75 %	24.02	1.64	64.34	7.03	0.18	0.82	1.76	2.06	0.02
100 %	22.23	1.92	66.76	7.66	0.17	1.18	–	1.92	0.03

**Fig. 4.** Results of moisture for each type of mixture.

75 % and 100 % of RS/RSA-2 and 75 % of RS/RSA-1. The average percentage of open porosity was 27 % $\pm$ 1 for the MP mixture, and higher percentages were observed for mixtures containing 100 % RS/RSA-1 (30 % $\pm$ 0.4), 75 % RS/RSA-2 (31 % $\pm$ 0.5), and 100 % RS/RSA-2 (33 % $\pm$ 0.1). The percentage of open porosity increased due to higher humidity in the specimens, which generates voids when evaporated after heating the samples.

Evidence suggests that RS waste experiences volume expansion due to the presence of cristobalite, as well as elevated silica levels, which, as indicated by Cruz (1987) and Davila (2008), contribute to this volumetric increase. Both the MP samples and the RS/RSA-1 waste exhibited escalating SiO₂ content, leading to an enlargement in linear dimensions compared to the RS/RSA-2 waste. Linear dimensional variations of up to

1 % are deemed acceptable, as values surpassing 1 % can induce cracks and/or catastrophic failures in the matrix, substantially diminishing the mechanical strength of the samples. Linear dimensional variations were up to 0.5 % for all mixtures (MP $\sim$ 0.4 %, RS/RSA-1 $\sim$ 0.20 %, RS/RSA-2 $\sim$ 0.10 %).

3.2.4. Cold crushing strength for the mixtures dried at 110 °C and treated at 1400 °C

The MP showed a greater strength gain in samples dried at 110 °C compared to samples treated at 1400 °C, in comparison to the gain for waste-containing mixtures, that have already undergone thermal treatment (Table 6).

In the samples dried at 110 °C, the MP exhibited cold crushing

Table 6

Results for density, water absorption, percentage open porosity, linear dimensional variation of the specimens, and cold crushing strength.

Reference	MP	RS/RSA-1			RS/RSA-2		
		25 %	75 %	100 %	25 %	75 %	100 %
Density (g/cm ³)	2.15 ± 0.07	2.25 ± 0.06	2.30 ± 0.12	2.15 ± 0.01	2.32 ± 0.01	2.13 ± 0.01	2.08 ± 0.01
Water absorption (%)	13 ± 1	12 ± 1	11 ± 2	14 ± 0.3	10 ± 0.01	15 ± 0.3	16 ± 0.2
Open porosity (%)	27 ± 1	26 ± 2	25 ± 4	30 ± 0.4	23 ± 0.08	31 ± 0.5	33 ± 0.1
Linear dimensional variation (%)	0.48 ± 0.1	0.16 ± 0.2	0.23 ± 0.03	0.05 ± 0.09	0.12 ± 0.09	0.08 ± 0.08	−0.04 ± 0.02
Cold crushing strength (dried at 110 °C, MPa)	23 ± 3	32 ± 1	31 ± 2	24 ± 2	23 ± 5	20 ± 0.5	20.5 ± 0.5
Cold crushing strength (treated at 1400 °C, MPa)	47 ± 4	35 ± 12	53 ± 15	26 ± 4	23 ± 3	21 ± 3	21.5 ± 2

strength of $\sigma = 23 \text{ MPa} \pm 3$, while the mixtures with waste 25 %RS/RSA-1 ($\sigma = 32 \text{ MPa} \pm 1$), and 75 %RS/RSA-1 ($\sigma = 31 \text{ MPa} \pm 2$) showed similar and higher strengths, as shown in Fig. 5a,b. This increase in strength occurred because the mixtures had a lower percentage of open porosity associated with lower moisture content as the fines content increased.

After firing at 1400 °C, there was an increase in the resistance only in the 75 %RS/RSA-1 mixture ($\sigma = 53 \text{ MPa} \pm 30$) compared to the MP ($\sigma = 47 \text{ MPa} \pm 4$) as shown in Fig. 5a. The notable variation in the specimens occurred because certain samples were prepared on days when the room temperature was approximately 30 °C. The temperature, in combination with the moisture content, can impact the hydration of aluminous cement (Dovál et al., 2006). According to Lee et al. (2013), and Rodger and Double (1984), room temperature values exceeding 25 °C might impede the formation of hydrates and influence the quantity and type of hydrates formed. These variables can result in a significant decrease in the strength of green samples and subsequently in samples sintered at high temperatures. Due to the high temperature and humidity, the moisture content experienced a considerable increase during mixing, leading to an acceleration in cement hydration. This accounts for the considerable variation in cold crushing strength observed among the 75 % RS/RSA-1 mixture.

In the case of the 25 % RS/RSA-1 and 100 % RS/RSA-1 mixtures, the resistance after firing at 1400 °C was lower compared to that of the MP. This can be attributed to the increased pore volume present in these mixtures. Furthermore, the elevated waste content, particularly in the case of 100 % RS/RSA-1, resulted in a higher proportion of the cristobalite phase. This, in turn, weakened the matrix of the test specimens after firing at 1400 °C. The presence of cristobalite introduces heightened stress into the material, leading to the development of cracks and fissures due to volume variation during the heating and/or cooling of the specimen, decreasing the cold crushing strength of the specimens (Krause, 2014).

When wastes with higher Fe content (RS/RSA-2) were introduced, specimens that were dried at 110 °C and fired at 1400 °C exhibited lower cold crushing strength in comparison to the MP. Following the drying process at 110 °C, the outcomes did not display significant variation ($p = 0.11$) when compared to the MP. The MP showcased a strength of $\sigma = 23 \text{ MPa} \pm 3$, and the average strength achieved with the inclusion of the wastes was $21 \text{ MPa} \pm 2$, as depicted in Fig. 5b. This outcome can be attributed to the slight rise in the percentage of porosity as the waste

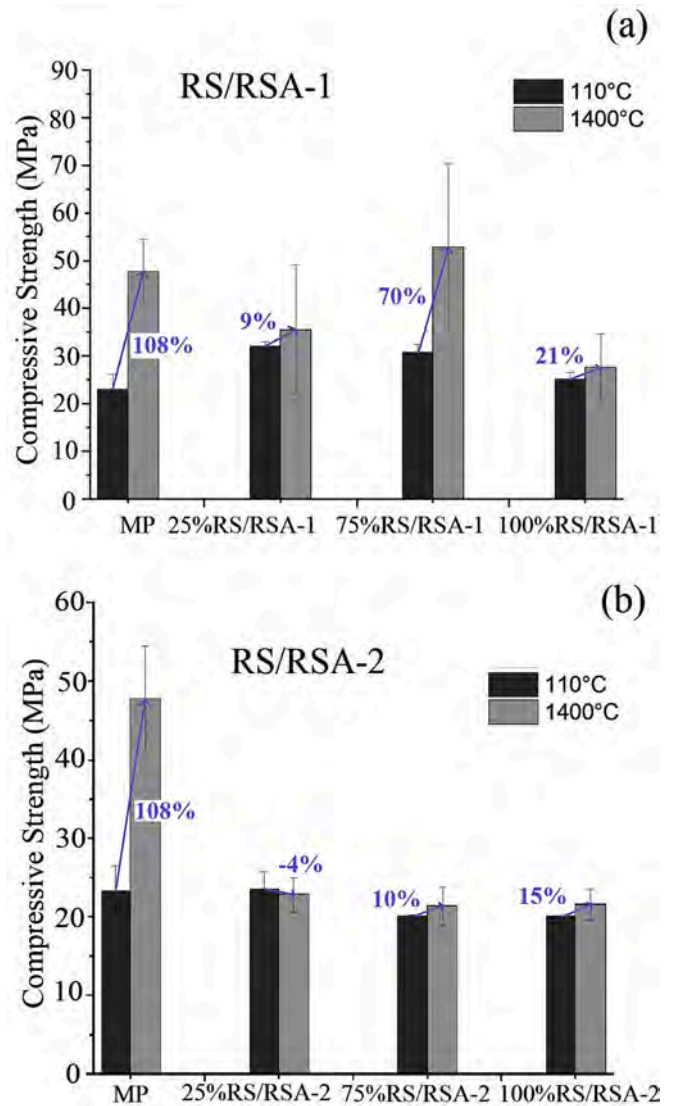


Fig. 5. Cold crushing strength for compositions with 0, 25, 75, and 100 % after drying at 110 °C and treatment at 1400 °C for RS/RSA-1 (a); and RS/RSA-2 (b).

content increased. This increase was a result of the higher water content in the mixture to achieve improved workability, thereby leading to a non-significant escalation in porosity following the sample drying process (De Castro and Pandolfelli, 2009).

A more significant reduction in cold compressive strength was observed for RS/RSA-2 after firing at 1400 °C. This observation could be linked to the presence of the liquid phase induced by the higher alkali content in RS/RSA-2 wastes, along with the increased CaO content, which diminishes the refractoriness of the mixture. The resulting liquid phase did not adequately counterbalance the material's expansion, which was promoted by the introduction of the waste. This rise in waste content has the potential to induce the formation of cracks or fissures due to the material's behavior, particularly with the escalated presence of the cristobalite phase post-incorporation (Krause, 2014; Oliveira et al., 2018). All mixtures exhibited a cold crushing strength and density in accordance with market requirements ($\sigma \geq 10 \text{ MPa}$).

Fig. 6 depicts the presence of the glassy phase in the MP, associated with a higher percentage of SiO₂ (22 %). In silico-aluminous refractory concrete, silica percentages above 16 % can result in minor amounts of glassy phase. The thermal treatment at 1400 °C led to a reduction in the quantity and size of pores. Following the sintering of the samples, the surface tension of the material contributed to a higher quantity of cracks

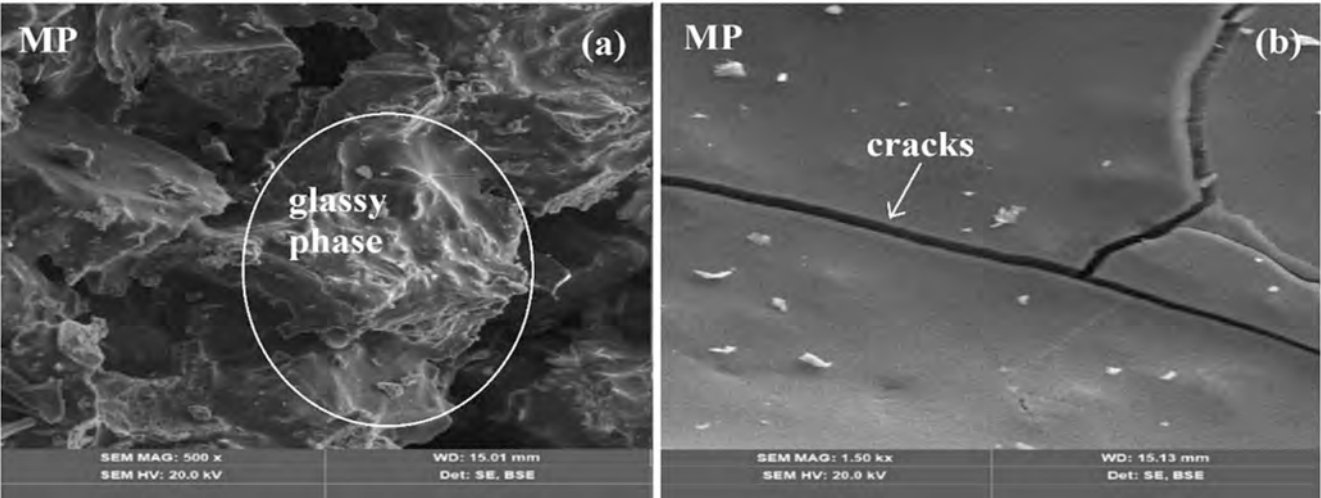


Fig. 6. SEM images of the MP microstructure after firing at 1400 °C: (a) 500x and (b) 1500x.

and/or fissures in the microstructure (Fig. 6b), rendering it more brittle and consequently diminishing the mechanical strength of the samples. A similar behavior occurred for mixtures with wastes.

Chen et al., (2023) investigated a structural optimization of the trial $\text{Al}_2\text{O}_3\text{--MgO}$ pre-cast bricks after server cycles in the ladle, through residual thickness. The optimized displayed a $\sim 30\%$ improvement in corrosion resistance after industrial application when compared with the conventional. It was attributed to the corroded behaviors and slag infiltration behaviors of Al_2O_3 -based aggregates in the corroded interface. The use of Al_2O_3 -based wastes, such as the residues of this study, can also increase the lifetime of linings.

3.2.5. Slag attack resistance test

The resistance to slag attack (Fig. 7) was assessed on all specimens fired at 1400 °C. The specimens underwent an acid slag test. Despite the test’s limited representativeness, it was conducted to demonstrate that the incorporation of wastes does not compromise the integrity of the specimens after exposure to high-temperature heating. Slag from induction and channel furnaces typically transform into non-reactive slag as it aims to achieve chemical equilibrium.

Based on the test results and sample analysis, varying degrees of attack were observed. Capillary penetration through the pores was evident in the less dense bodies, where specimens exhibited a higher percentage of pores. Consequently, it can be inferred that one specimen was more susceptible to slag attack than the other due to its elevated porosity index resulting from waste incorporation, as compared to the

standard mass.

4. Conclusion

Wastes from silico-aluminous refractories from induction furnaces and casting ladles from the foundry process can be repurposed to develop new materials for the refractory hydraulic binder for the lining. This waste is classified as Class IIA Non-Inert waste and is not considered hazardous.

Commercial refractory patch mass is a material composed mainly of SiO_2 , Al_2O_3 , and CaO , with a silica content of 60 wt%. It starts melting at a temperature close to 1200 °C. Siliceous-refractory wastes can be used as a priority source of silica, while silico-aluminous refractory waste can provide silica, alumina, and calcium oxide. The iron content in the mixtures containing the waste studied was lower than that in the commercial refractory patch mass (MC), but the alkali contents were higher. The mechanical separation process did not significantly change the thermal behavior of the materials.

The inadequate cleaning of the liquid bath, the high temperature of the liquid metal, the type of slag in the liquid bath, the thickness of the refractory material in the ladles, ladle maintenance, operational skill, and the purity of raw materials are additional variables that influence the refractory performance. The granulometric distribution curve and the particle morphology of the waste and commercial refractory patch mass were similar, making the waste suitable for use in terms of conformation. The control refractory patch mass (MP) exhibited a cold

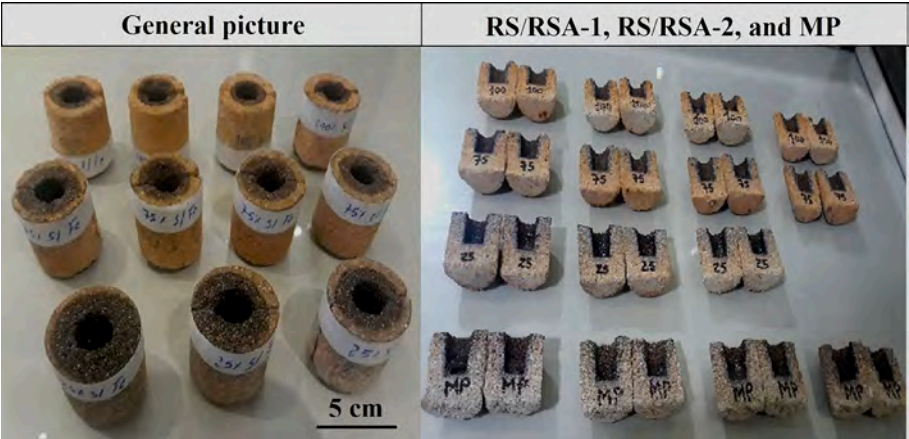


Fig. 7. Aspect of specimens after slag attack resistance test for MP, RS/RSA-1, and RS/RSA-2.

crushing strength and density in accordance with market requirements ($\sigma \geq 10$ MPa and $\rho \geq 2.10$ g/cm³). The incorporation of waste materials facilitated strength enhancement. This effect can be attributed to improved particle size dispersion in the fine fraction and a reduction in the coarse fraction, leading to an increase in sample packing density. Greater densification reduces the penetration of slag and liquid metal during heating.

The use of waste not only reduces costs for the company but also reduces environmental impact and improves the sustainability of the production chain. The partner company in this study utilized 16 tons per month of refractory patch mass for lining in 2022, resulting in a total cost of USD 222,613.29. The findings presented in this research demonstrate the potential to replace 25 % by volume of the commercial refractory patch mass with siliceous and silico-aluminous waste, leading to savings of USD 55,653.32 per year (after the implementation costs of the grinding system have already been absorbed). However, the biggest gain of the project for the company is in the environmental policy, the sustainability of the production chain, and recognition by customers and the Community. The analyzed wastes generated by the foundry industry have acceptable properties to be reused as refractory hydraulic binders for lining.

CRediT authorship contribution statement

Maria de Lourdes dos Santos Schackow: Conceptualization; Data curation; Formal analysis; Investigation; Methodology. Validation; Visualization; Roles/Writing - original draft. **Adilson Schackow:** Writing - review & editing, Writing - original draft, Visualization, Validation, Methodology, Investigation, Formal analysis. **Karoline Bastos Mundstock:** Validation, Data curation. **Marilena Valadares Folgueras:** Conceptualization; Formal analysis; Investigation; Methodology; Project administration; Resources; Supervision; Validation; Visualization; Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.clema.2024.100228>.

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