EXECUTIVE SUMMARY

This work reports the incorporation of industrial wastes in the production of lightweight aggregates of expanded clay, often used as a building material in the construction industry. The analysis has been focused upon wastes from the casting and paper pulp industries and also on those from urban and industrial wastewater treatment plants.

Such wastes are mostly composed of oxides like SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MgO, K$_2$O, amongst others. As such, they were evaluated as a partial substitute of traditional raw materials in the lightweight aggregate manufacturing, with obvious economical and environmental benefits. In addition, the effect of wastes incorporation in enhancing the expansion properties of alternative clay materials was evaluated.

For this purpose, both the wastes and raw materials were characterized for their chemical and physical properties. Toxicological behavior of the wastes was also evaluated. Furthermore, the processing conditions were optimized at a laboratory scale. The loss on ignition (at 900 °C) and the expansion capability were assessed for the various formulations (clay/wastes) prepared.

Subsequently, the incorporation of wastes into the production of lightweight aggregates was carried out in large scale industrial trials. These tests were used to validate, from a technical and environmental point of view, the accuracy of the laboratory results. In total, 8 separate industrial runs were performed in fully operational mode regarding the incorporation of various wastes into the clay based matrixes: green liquor dregs, slaker grits, steel shot blasting dusts, sludges from the wastewater treatment resulting from different processes and biomass ashes.

Each waste was tested for a single level of incorporation. The exact level varied between 1 and 5%, according to the waste, and was based upon the results previously obtained at the laboratory trials. The wastes were incorporated during the preparation stage.
The resulting formulations of clay/waste, with the addition of expanding agents, were introduced into a rotating furnace, dried and fired under normal operating conditions (1170 °C). In the course of this process, the gaseous emissions were monitored for those compounds legally enforced and others considered relevant for the correct operation of the plant, depending upon the specific characteristics of the waste. By direct comparison with the continuous data of the gaseous emissions under normal operation, it can be concluded that the addition of wastes in the clay matrix does not induce any specific contamination.

The lightweight aggregates of expanded clays, were characterized for their mechanical properties: compression strength and density. It was observed that with waste incorporation, and within the incorporation levels tested, the product complies with the required technical specifications.

The environmental evaluation of the aggregates shows that these may be classified as inert material, according to the legal criteria for landfilling. Furthermore, the majority of the formulations tested is similar to those of traditional clays and are well within the content variability for the inorganic compounds that are usually present in their composition.

From the industrial tests, one may conclude that the incorporation of various wastes into the manufacture of expanded clays is an environmentally and economically sound procedure.

From a technical point of view, the procedure is feasible requiring negligible adaptations to the production methods. In addition, because the wastes are alternative raw materials, a smaller amount of virgin raw materials will be required for the same production output.

INTRODUCTION

Wastes coming out of any industrial activity are of varying hazardousness degree, which require appropriate routes for their management. Whatever the option followed, it must be environmentally acceptable and economically competitive. Preferably it could also be a source of revenue. Therefore, waste management is of prime concern for all those involved who must comply with the existing legislation. This values the options that reduce the amount of waste or their treatment.

In this way, the environmental priorities concerning recycling and waste valorization are the most attractive. This last option includes both the energy valorization and material recovery. However the non existence of technically sound alternatives for an adequate waste treatment that can address these challenges makes landfilling the route most often used. This is clearly the least desirable option from both the environmental and economical points of view.

Over the years various studies have been carried out in order to develop technologies for the valorization of inorganic wastes through their incorporation in clay based materials for the construction industry. Various projects [1,2] have addressed this issue and a national patent (102597) has been awarded [3]. The main mechanisms present in the inertization of phases with high levels of heavy metals present in wastes in clay-based ceramics have been described [4,5,6].

Other technologies developed with success include the utilization of blast furnace slags, fly ash, scrap tire rubber, waste polyethylene terephthalate (PET) bottles and biological sludges from the paper industry, in the production of lightweight aggregates of concrete [7,8,9] or expanded clay [10] for structural applications.
Although the Technologies summarized above are adequate processes for treatment of specific classes of wastes, it is of great relevance the search for alternatives that will enable the valorization of wastes from various industrial sectors. In this context the project RES2ARGILA aimed to validate at an industrial level the incorporation of a wide variety of industrial wastes in the production of lightweight aggregates of expanded clay, which is a widely used construction material. This project was co-sponsored by the ADI (Portuguese Innovation Agency) and the industrial partner Maxit - Tecnologias para a Construção, Reabilitação e Ambiente S.A. CVR - Centro para a Valorização de Resíduos and TecMinho – Associação Universidade Empresa para o Desenvolvimento acted as the technical partners for the Project.

The development of the project was centered in assessing the substitution of a fraction of the raw materials by industrial wastes and the application of non conventional clays. These may not exhibit the required plasticity and expansion capability that are required for the fabrication of the expanded clays but may be enhanced by the addition of appropriate wastes. For this purpose, both the wastes and the various clays were tested and characterized in the laboratory and their blending subsequently optimized. The follow up industrial trials assessed the emission levels produced and the quality of the final materials, enabling the validation of the technology developed and allowing, according to legal requirements, its subsequent implementation at an industrial scale. This comprehensive study enabled the selection of appropriate combinations of wastes and alternative clays that guarantee a high quality product and also may contribute to the reduction of wastes that are often deposited in landfills. Thus, it is an environmentally and economically attractive process.

CHARACTERIZATION OF THE WASTES AND RAW MATERIALS

In the early stages of this project, once the various wastes were selected as viable candidates for the incorporation in the fabrication process of lightweight aggregates of expanded clays, they were characterized for their physical, chemical and toxicological properties. The selection included: steel shot blasting dust (SBD), green liquor dregs (DRG), slaker grits (GRT), biomass ashes (ASH), sludges from wastewater treatment resulting from aluminium anodising processes (SAA), from steel pickling processes (SSP), from galvanic processes (SG), sludges from urban wastewater treatment (SU), slags (SLG), refractories (RFT), greensand (GSD) and core sand (CSD). In addition, samples of clays were also characterized. They were sourced from the company own quarries and also from external suppliers.

From the chemical characterization, carried out by X ray fluorescent spectrometry (FRX), it was observed that the wastes selected included in their composition compounds such as SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MgO, K$_2$O, amongst others. Because these compounds are also present in the standard clay matrix, it can be concluded that they are suitable as an alternative raw material and therefore may be included in the formulation of aggregates of expanded clay. The characterization of clays enabled the selection of the most adequate matrixes for subsequent testing.

From the physical point of view, the moisture level, particle size distribution, density and surface area suggest that the majority of the wastes may be directly incorporated into the clay matrix without further preparation. This is of great economical advantage because it reduces the processing costs.

The toxicological behavior of the wastes was assessed through a leaching process, carried out according to standards DIN 38414-S4 [11] or EN12457-4 [12], followed by an analysis of the leaching solution. The results show that most of the wastes are inert and non hazardous for landfill disposal. In fact only the galvanic sludges from industrial waste water treatment may be classified as hazardous.
OPTIMIZATION OF THE INCORPORATION AND PROCESSING TECHNOLOGIES: LABORATORY TESTS

The initial stages of the tests at a laboratory scale aimed at identifying both the processes and equipments most suitable for the pre treatment of the wastes and also at the methodologies for their incorporation. Based upon the physical characteristics of the wastes that were selected for the current study, it was concluded that the slags and refractories from the casting industry required an additional treatment. A milling and a separation operation enabled the fragmentation of the particles into a size more appropriate for processing and the separation of the metallic part.

Although most of the wastes did not require any specific operation, a uniform mixing of the wastes with high moisture levels with the matrix clays required the design and construction of a purpose built distribution box. With this device a correct distribution of the materials on the conveyor belts during the loading phase is guaranteed.

The overall design of the layout for the incorporation of the wastes into the clays has taken into account various factors: characterization of the various materials, the required pre-treatments, the purpose built equipments and the compatibility to the existing industrial procedures in the industrial company. Figure 1 depicts the layout of the process that was proposed for the incorporation of the wastes into the fabrication of lightweight expanded clays. This approach reduces the disruption of the existing industrial process.

By incorporating the wastes into the load preparation stage (either as sludge or as dry particles) just upstream of the milling operation a good homogenization of the mixture is achieved.

Figure 1- Schematic representation for the incorporation of wastes in the processing of lightweight aggregates of expanded clay

Another important test carried out at a laboratory scale was the determination of the clay expansion capability (at 1170 °C) and the Loss of Ignition, LOI (at 900 °C), for the various combinations of wastes and raw materials. The incorporation level was based upon the chemical characteristics of the
various materials. All the tests were carried out at the laboratories of the industrial partner (Maxit), which included also the effect of the addition of expansion agents to the process.

For this purpose and for each single formulation a set of 10 specimens was built. They consisted of hand made spheres whose mass varied between 2.3 and 2.5 g. They were dried and pre heated at approximately 110 °C for a period of 2 h. Subsequently, the temperature was increased up to 200-250 °C and for a period of 1 h. Finally the specimens were heated in an oven for 8 h at 1170 °C. This enabled the complete expansion of the material which was determined by its density at that temperature. According to the criteria used by Maxit, the product is of high grade if the density is below 350 kg/m³.

Regarding the LOI (900 °C), clay samples (without any wastes) were dried at 110°C±5°C and placed in a crucible. This combination was weighted and introduced into an oven at 900 °C for a period of 15 min. Once removed and cooled its weight was determined and the LOI was calculated according to

$$\text{LOI}(X^\circ C) = \frac{M_1 - M_2}{M_1 - T} \times 100(\%)$$

being:

- $T$ - weight of the crucible
- $M_1$ - weight (before drying)
- $M_2$ - weight (after cooling)
- $X$ – testing temperature

The value for LOI should be below 10%.

Figure 2 shows the influence regarding the application of the wastes into the manufacture of expanded clays. The results are presented for the two most important criteria regarding its applicability as a construction material (density and LOI) as a function of the waste. Data obtained when oil (expanding agent) was not included is shown with a cross on top of the symbol. The figure also shows the boundaries required for a high grade product.
The results show that the critical parameter is often the density (the expansion ability) as, for most of the cases, the LOI limit is easily complied. In addition the use of expanding agents does not guarantee success, but depends upon the type of the clay. Another interesting feature is that the trends that improve one of the parameters work in opposite direction for the other parameter for most of the wastes.

When developing mixtures using sludges from wastewater treatment resulting from aluminum anodizing processes (SAA) various clays were tested. However it was observed that the waste incorporation level had to be kept below 1% with stock clay and adding oil as an expansion agent. However, adding sludges from wastewater treatment resulting from steel pickling processes (SSP) (rich in Fe$_2$O$_3$) in clays of low expansion capacity (such as the yellow clays) improves its expansion ability, although oil (1 %) is required as an expansion agent. Incorporation levels of 20% of (SSP) are needed to assure the use of such alternative clay (yellow clay) as a matrix for lightweight aggregates. This is based on the presence of iron compounds that promotes the pyroplastic expansion of clays through the partial reduction of iron oxide. This results in the formation of a gaseous phase, a prime vehicle for clay expansion. The incorporation of this residue in stock clays (at levels below 3%) enabled the use of oil as the expansion agent at levels below those traditionally used (0.5 %) without any loss of properties in the final product.

Figures 3 through 4 illustrate the effect of adding wastes into clays in its expansion capability and LOI. Figure 3 shows the LOI for the various wastes combined with the stock clay. The acceptable limit is also plotted. The results include the data when oil is added (full diamonds) and when oil is not included as an expanding agent (open squares). The data shows that the expanding agent is not paramount to achieve a LOI level below the tolerable limit. It appears that the type of waste has a stronger effect on the overall efficiency. The LOI data also suggests that Dregs (DRG) should be kept below a 2% level of incorporation.

![Figure 3 - Effect of waste on the LOI for a stock clay matrix.](image)

Figure 4 depicts the effect of the waste incorporated upon the density of the aggregate. The acceptable limit is also included in the plot. The data refers only the stock clay as matrix.

![Figure 4 - Effect of waste on the density of the aggregate.](image)
The results show that when oil is not used (open squares in Figure 4) the higher density can be problematic, except in the incorporation of the sludges from urban wastewater treatment (SU) even for incorporation levels of this waste up to 10%.

The results for the various formulations show that the stock clay (mixture of common red clays) is an appropriate matrix for incorporating wastes from the casting and paper pulp industries and also on those from industrial wastewater treatment plants, when in the presence of an expanding agent. For most of the wastes an incorporation level of 5% meets the required specifications. When incorporating steel shot blasting dust (SBD) and green sands (GSD), it is recommended that the incorporation level should be kept below 3%. Otherwise, the final product is mechanically fragile.

The various tests carried out at a laboratory scale coupled with the full characterization of the materials (wastes and clay matrixes) were used as a basis for planning a set of large scale industrial tests focused in the most promising combinations for the matrix clay and waste.

INCORPORATION OF INDUSTRIAL WASTES IN EXPANDED CLAYS: INDUSTRIAL TESTS

The production of lightweight aggregates by the incorporation of wastes in clay based matrixes has been tested at an industrial scale. These tests aimed to confirm and validate, from a technical and environmental point of view, the best compositions and the incorporation conditions selected at the laboratory scale as the most profitable. The assessment of the environmental impact caused by the incorporation of such wastes has been done by monitoring the critical parameters of the gaseous emissions from the industrial furnace and by performing leaching tests on the final products.

The clay/waste formulations tested at an industrial environment, are summarized in Table 1. Their selection has been based upon on the characteristics of the materials and on the laboratory results regarding the LOI (at 900 °C) and the expansion capability of the lightweight aggregates when wastes were incorporated. All the experimentations have been carried out at Maxit S.A., a plant that produces approximately 650,000 m³ per year of lightweight aggregates of expanded clay. In each trial a single
content of waste incorporation has been tested, always in the presence of an expanding agent that has been incorporated in the mixer.

Table 1 - Clay/waste formulations tested at an industrial scale in the manufacture of lightweight aggregates of expanded clay.

<table>
<thead>
<tr>
<th>Stock Clay (%)</th>
<th>Yellow Clay (%)</th>
<th>DRG (%)</th>
<th>GRT (%)</th>
<th>SSP (%)</th>
<th>SAA (%)</th>
<th>SU (%)</th>
<th>ASH (%)</th>
<th>SBD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2</td>
<td>-</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
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<td>100</td>
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<td>5</td>
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<td>2</td>
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<td>1</td>
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<td>-</td>
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<tr>
<td>100</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
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</tr>
</tbody>
</table>

In industrial trials, incorporations up to 5% of SBD, DRG, GRT, ASH, SAA, SSP and SU were blended into a clay based matrix composed of a mixture of common red clays used in normal processing (stock clay). Sludges from SSP were also incorporated in a distinct clay based matrix of a mixture of clays (stock and yellow) with distinct expansion capability. All these wastes have been incorporated in the clay matrixes before the milling stage, according to the methodology defined in Figure 1, until the desired incorporation level is achieved. Subsequently, the plastic formulations (clay/waste), with a moisture level of 21% and in the presence of mineral oil, were introduced in the rotary kiln, dried and fired at the standard operating conditions (1170°C) used for the production of lightweight aggregates.

The trials run for a period of approximately 12 hours, during which the gaseous emissions were periodically analyzed, for CO, NOx, SO2, HF, HCl, particle concentration and volatile organic compounds (VOC’s) contents. Sampling the gases was carried out according to standard methods. The gaseous emissions during the production of lightweight aggregates when wastes were incorporated into the clays were compared with those resulting from normal processing. The results show that no additional contamination was observed due to the incorporation of the wastes for the levels tested and, for some parameters, a reduction in their concentration is even observed. All the emission parameters evaluated during the trials show emission levels bellow the legal limits, excepted for those corresponding to the incorporation of sludges from wastewater treatment resulting from steel pickling processes (SSP) and of sludges from urban wastewater treatment (SU), both in a stock clay matrix. In these, the volatile organic compounds (VOC’s) is higher than the acceptable limits. However, this fact could not be linked to the waste presence but most likely to the expanding agent used (2% oil mixed with water) in the manufacturing process.

The lightweight aggregates of expanded clay produced in the course of the industrial experiments have been characterized for its compression strength and density. The results (Table 2) show that the aggregates meet the specified values for commercial lightweight expanded clay: density below 500 kg/m³ and a compression strength >0.9 MPa.
Samples of the aggregates produced have also been collected during the industrial trials in order to determine its leaching behaviour. This is an important test to assess its long term environmental impact. For this purpose a leaching procedure, according to EN 12457-4 [12] has been followed. Once filtered, the leaching solution was analyzed for the most relevant parameters and compared to the concentration limits indicated by European Council Decision 2003/33/CE [13]. The results obtained enable its classification, for disposal purposes, as inert materials.

Based on the characterization of the final products, it may be concluded that when wastes are incorporated, for the content and clay matrixes tested, the fired products meet the properties requirements for such materials making them compatible with construction applications. Simultaneously, all the aggregates have been classified as inert materials, for the disposal, presenting no environmental limitations or impact.

Table 2 – Characterization of the lightweight aggregates of expanded clay produced during the industrial trials

<table>
<thead>
<tr>
<th>Waste/ incorporation (%)</th>
<th>Clay Matrix</th>
<th>Compression strength (6.3-10mm) ≥ 0.9 MPa</th>
<th>Density 250-500 kg/m³</th>
<th>Environmental Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>DRG / 2%</td>
<td>Stock</td>
<td>1.5</td>
<td>405</td>
<td>Inert</td>
</tr>
<tr>
<td>GRT / 5%</td>
<td>Stock</td>
<td>1.3</td>
<td>440</td>
<td>Inert</td>
</tr>
<tr>
<td>SSP / 4%</td>
<td>Stock</td>
<td>1.0</td>
<td>373</td>
<td>Inert</td>
</tr>
<tr>
<td>SSP / 2% Stock + Yellow</td>
<td>Stock</td>
<td>1.1</td>
<td>438</td>
<td>Inert</td>
</tr>
<tr>
<td>ASH / 2%</td>
<td>Stock</td>
<td>1.2</td>
<td>360</td>
<td>Inert</td>
</tr>
<tr>
<td>SAA / 1%</td>
<td>Stock</td>
<td>0.96</td>
<td>330</td>
<td>Inert</td>
</tr>
<tr>
<td>SBD / 1%</td>
<td>Stock</td>
<td>1.0</td>
<td>351</td>
<td>Inert</td>
</tr>
<tr>
<td>SU / 5%</td>
<td>Stock</td>
<td>1.1</td>
<td>404</td>
<td>Inert</td>
</tr>
</tbody>
</table>

Regarding the product morphology, only with the incorporation of grits (GRT) it was observed the presence of calcium carbonate contaminations in the expanded clay. This leads to the embrittlement of the material. All the remaining aggregates present a colour and morphology similar to those exhibited by the products in the absence of wastes (Figure 5).

Figure 5 – View of the lightweight aggregates produced in industrial trials
TECHNICAL AND ENVIRONMENTAL EVALUATION

From a technical point of view, the quality of the expanded aggregates and their full compliance with the environmental specifications, proved that the technology developed is viable. This is achieved with a minimum of changes in the traditional manufacture process of lightweight aggregates of expanded clay. Only for the stage of load preparation it has been identify the need to introduce an additional equipment in order to assure the correct incorporation of wastes with high moisture content: the sludge distribution box. This equipment has been developed and built in the course of the present project. It is also anticipated that a dosing device is necessary to feed the wastes (as sand, fines and dust) into the load preparation stage.

Only for slags and for mixtures of slags and refractories the application of a pre-treatment of milling, separation and particle size classification was pointed as necessary to ensure their efficient incorporation in the process.

For all the wastes tested, their mixing with the clay matrixes was effective when performed under the conditions normally prevailing in the production of lightweight aggregates of expanded clay. Additionally, the quality of the gaseous emissions produced and the characteristics of the expanded final product indicate that operational conditions of drying and firing followed in the common process are also applicable in the production of aggregates with wastes incorporation.

In addition, the economical evaluation of the developed technology was carried out. It has been estimated that its application could result in the handling of up to 30% of the 400,000 ton/year of wastes that are presently land filled (50 €/ton). Assuming that the average content of wastes incorporation can reach the level of 3%, and that the consumption of raw materials reaches 300,000 ton/year, the economic benefit will be of 450,000 €/year. Additionally there is the economic benefit regarding the replacement of a fraction of the raw materials and the use of clay matrixes of a lower cost without any penalty in the final product.

As far as capital costs associated with the technology, one has to consider the dosing device, previously referred, used for the incorporation of sands and dusts. For the sludge incorporation, no indirect costs have been determined since the wastes are directly discharged in the sludge distribution box. The economical viability of incorporating slags and refractories has also been evaluated, considering the need to set up a unit for the pre-treatment of such wastes. The estimated cost associated to its treatment was of 4.6 €/ton, which is significantly less than the cost of waste disposal at landfills for inert materials - 9 €/ton.

CONCLUSIONS

The incorporation of various wastes in matrixes clays for the production of lightweight expansion clays resulted in inert, materials with physical and mechanical characteristics which are compatible with the demands required by the market. In addition, the resulting gaseous emissions during the firing operation are well within the legal limits applicable to such industries. In brief the technology is sound and requires negligible adaptations to the normal processing.

The use of wastes enabled a partial substitution of traditional raw materials and also the utilization of alternative raw materials as the product matrix. This is the case for the clays with a low expansion ability which are traditionally outside the scope of such applications.
This technology is also an important method for the management of some industrial wastes, being paramount in terms of environmental protection. Therefore it is expected that it may have an important contribution to waste management. The costs associated with this technology are low when compared with those associated with waste landfill, making it competitive from the economic point of view.

The industrial validation of the technology was an important step in the overall assessment for the implementation at an industrial scale of the process. From these tests it was concluded that it may be used as an inertization process for wastes from a wide variety of industrial sources.

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