

## Close the loop in ceramic industry

### Introduction

Europe needs to move away from a 'linear' economic model that is resource intensive and unsustainable towards a more 'circular' approach, where the value of products, materials and resources is maintained in the economy for as long as possible, and the generation of waste minimized. This transition is an essential requirement to ensure a sustainable, low carbon, resource efficient and competitive economy.

The aim of "closing the loop" of product lifecycles through greater recycling, by safely turning waste byproducts from an industry into useful secondary resources for another industrial sector, is strongly encouraged by current European Union policies, towards industrial symbiosis, ample coordination and circular economy.

Secondary resources i.e. end of life products, industrial side streams and wastes, are the "wasted resources of today", if they are not utilized and returned for use. The primary design strategies for Residue utilization must aim to reduce, cost, waste and energy and can be implemented with innovative production and manufacturing technologies, industrial symbiosis practices and end use solutions crossing the industrial sectors.

As to material re-use, the European orientations resulting from the VI Environmental Action Programme suggest the match between sustainable use of resources and sustainable management of waste, which is the key for Greece to recover from crisis. Therefore, to implement sustainable waste management, the best processing and re-use technologies, in full consideration with the "production proximity" principle, must be taken into account. An increase in re-use, not only will reduce the demand for raw materials, but also boost the re-use of valuable materials, now discarded as waste and lead to a mitigation in energy consumption and greenhouse gas emissions, generated by raw materials extraction and processing.

Business models aiming to use waste as a resource promote cross-sector and cross-cycle links by creating markets for secondary raw materials. These can reduce the use of energy and materials during production and use facilitating locally clustered activities to prevent by-products from becoming wastes: industrial symbiosis. Positive economic effects can arise from the availability of cheaper materials diverted from waste as an alternative to virgin materials, including avoiding the costs of waste disposal and capturing the residual economic value of existing material streams. Positive environmental effects come from a net reduction in environmental pressure from waste disposal and the production of virgin materials.

Social effects include the reduction of municipal waste disposal and other environmental costs. Recycling chains that meet environmental and labor safety standards have positive social impacts, but lock-in effects can occur if the demand for waste as an input reduces the incentive for waste prevention.

Sustainable waste management implies not only the quantitative prevention and reduction of hazardous waste but also a greater recourse to energy and material inertisation and re-use. Downgrading the danger class of wastes or converting them to proper new raw materials, means moving from a traditional linear growth model, based on "take, produce, consume and dispose", to a circular self-sustaining model where resources remain inside the economic system until their end-of-life in order to be reused several times for production purposes, thus generating new value.



## The Ceramic Industry

Huge quantities of clays per year needed for the production of considerable amounts of fired ceramic bricks worldwide, and therefore much research focuses on the utilization of alternative raw materials from various origins into clay mixtures, at different combinations and proportions, for the fabrication of conventional sintered bricks.

There are opportunities to use Materials from Alternative, Recycled and Secondary Sources to manufacture bricks; however, the benefits of this approach must be carefully balanced against potential implications on product durability, performance specifications, and other logistical and environmental considerations.

The ceramic industry is important for the European economy (€28 bn production value; 200,000 direct jobs; €4.6 bn positive trade balance; 80% SMEs) and a leading technological sector. Technological innovation in the ceramic industry has been deeply changing the manufacturing cycle and the requirements for raw materials. Classic categories are practically useless to estimate the effective potential of industrial minerals for ceramics and to reveal possible criticalities. Besides the growing concern on waste recycling, a recognized approach to assess the actual potential of residues as ceramic raw materials is still lacking.



To reach circular economy, this industry has invested in several innovations, such as, the reuse of roof tiles, the recycling of ceramic materials from construction and demolition waste, crushed and used as secondary raw materials for different applications. However, for these options to be viable there must be an adequate access to raw materials as well as separation and processing of waste and a well-functioning market for secondary raw materials.

The scientific applied research on technologies and materials concerning heavy clays industry can lead to sustainable social, economic and environmentally - friendly solutions for inorganic industrial waste management, based on the thermal process of sintering (firing) which takes place during the brick production.

Sintering of ceramic materials is the method involving consolidation of ceramic powder particles by heating the "green" compact part to a high temperature below the melting point, when the material of the separate particles diffuse to the neighbouring powder particles. During the diffusion process the pores, taking place in the "green compact", diminish or even close up, resulting in densification of the part, improvement of its mechanical properties. The most critical factors in the process are chemical nature and initial density of the material, particle size, pressure, time and heating cycle, atmosphere inside the furnace (reducing or oxidizing). As to waste processing, the major benefits are volume reduction, production of a highly compacted material, which is extremely weather-resistant, with run-off reduction. Controlled heating leads to the final immobilization and inertisation of dangerous compounds contained in waste, namely largely used to incorporate heavy metals in ceramic materials. The new output materials used in the building sector as roof tiles, bricks, tiles, etc. It is also possible to manufacture glass - ceramic products or porcelain tiles that due to the higher glass content offer better stabilization conditions for the toxic waste components.

## Case study

Since 2011 the "Laboratory of Chemical Technology, Science and Mechanical Behavior of Materials" at the Technological Educational Institute of Thessaly, cooperates in research programs with the bricks and tiles industry "TERRA S.A.", on the valorization of various types of wastes as substitutes to clayey raw material. The

research co-financed by either “TERRA S.A.” or the public sector and European funds. Different types and proportions of inorganic and organic wastes tested as substitutes to the clayey raw material. The prerequisites of reuse/recycling of the different waste streams in the clayey raw materials in terms of the final ceramic product are:

- Uniform quality and availability of the residues in case used on a large scale
- Technically at least as good as the virgin materials for which they substitute
- Final ceramic products with the same or better performance compared to the original
- Environmentally acceptable final ceramic products causing no danger to human health

Additionally different sintering temperatures tried in order to investigate the possibility of energy saving.

Extruded and pressed specimen produced and the quality of the produced ceramics evaluated by measuring the following properties:

1. Water absorption
2. Porosity
3. Thermal conductivity
4. Mechanical properties (3 point bending and Brazilian test)
5. Freeze thaw test (for extruded specimen)

Additionally, during the thermal process, real time measurements realized on:

1. Produced flue gases ( $O_2$ , Cl, F,  $C_xH_y$ ,  $CO_2$ , CO,  $NO_x$ ,  $SO_x$ )
2. Consumed energy

Leaching tests performed on the final products, predicted the concentrations of the heavy metals in the leachate for the assessment of their environmental behavior over their life cycle. Finally, the microstructure of the final products examined by using SEM.

The used wastes and the research results are presented in the following table.

A/A	Waste	Results - Benefits
1.	Mill Scale	Specimens had satisfactory physico-mechanical properties by adding the waste up to 6%. Insulation properties improvement: YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/> Energy saving during sintering process: YES <input type="checkbox"/> , NO <input type="checkbox"/> , N/A <input checked="" type="checkbox"/> Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/> Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/> , NO <input type="checkbox"/> , N/A <input checked="" type="checkbox"/>
2.	Municipal Wastes Sewage Sludge	Specimens had satisfactory physico-mechanical properties by adding the waste up to 6%. Insulation properties improvement: YES <input checked="" type="checkbox"/> , NO <input type="checkbox"/> , N/A <input type="checkbox"/> Energy saving during sintering process: YES <input checked="" type="checkbox"/> , NO <input type="checkbox"/> , N/A <input type="checkbox"/> Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/> Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/>
3.	Pet coke	Specimens had satisfactory physico-mechanical properties by adding the waste up to 6%. Insulation properties improvement: YES <input checked="" type="checkbox"/> , NO <input type="checkbox"/> , N/A <input type="checkbox"/> Energy saving during sintering process: YES <input checked="" type="checkbox"/> , NO <input type="checkbox"/> , N/A <input type="checkbox"/> Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/> Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/> , NO <input type="checkbox"/> , N/A <input checked="" type="checkbox"/>
4.	Scrap soil	Specimens had satisfactory physico-mechanical properties by adding the waste up to 6%.

		<p>Insulation properties improvement: YES <input checked="" type="checkbox"/>, NO <input type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Energy saving during sintering process: YES <input type="checkbox"/>, NO <input type="checkbox"/>, N/A <input checked="" type="checkbox"/></p> <p>Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/>, NO <input type="checkbox"/>, N/A <input checked="" type="checkbox"/></p> <p>Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/>, NO <input type="checkbox"/>, N/A <input checked="" type="checkbox"/></p>
5.	EAFC	<p>Specimens had satisfactory physico-mechanical properties by adding the waste up to 3%.</p> <p>Insulation properties improvement: YES <input type="checkbox"/>, NO <input checked="" type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Energy saving during sintering process: YES <input type="checkbox"/>, NO <input type="checkbox"/>, N/A <input checked="" type="checkbox"/></p> <p>Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/>, NO <input type="checkbox"/>, N/A <input checked="" type="checkbox"/></p> <p>Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/>, NO <input type="checkbox"/>, N/A <input checked="" type="checkbox"/></p>
6.	Mill Scale & Sewage Sludge	<p>Specimens had satisfactory physico-mechanical properties by adding the waste up to 6% for mill scale &amp; 3% for sewage sludge.</p> <p>Insulation properties improvement: YES <input type="checkbox"/>, NO <input checked="" type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Energy saving during sintering process: YES <input checked="" type="checkbox"/>, NO <input type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/>, NO <input checked="" type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/>, NO <input checked="" type="checkbox"/>, N/A <input type="checkbox"/></p>
7.	Scrap soil & Sewage Sludge	<p>Specimens had satisfactory physico-mechanical properties by adding the waste up to 6% for scrap soil &amp; 3% for sewage sludge.</p> <p>Insulation properties improvement: YES <input checked="" type="checkbox"/>, NO <input type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Energy saving during sintering process: YES <input checked="" type="checkbox"/>, NO <input type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/>, NO <input checked="" type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/>, NO <input checked="" type="checkbox"/>, N/A <input type="checkbox"/></p>
8.	EAFC & Sewage Sludge	<p>Specimens had satisfactory physico-mechanical properties by adding the waste up to 3% for EAFC &amp; 3% for sewage sludge.</p> <p>Insulation properties improvement: YES <input checked="" type="checkbox"/>, NO <input type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Energy saving during sintering process: YES <input checked="" type="checkbox"/>, NO <input type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/>, NO <input checked="" type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/>, NO <input checked="" type="checkbox"/>, N/A <input type="checkbox"/></p>
9.	Olive - mill wastewater	<p>Specimens had satisfactory physico-mechanical properties by adding the waste instead the water needed to prepare the plastic mass (approximately 18%).</p> <p>Insulation properties improvement: YES <input checked="" type="checkbox"/>, NO <input type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Energy saving during sintering process: YES <input checked="" type="checkbox"/>, NO <input type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/>, NO <input checked="" type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/>, NO <input type="checkbox"/>, N/A <input checked="" type="checkbox"/></p>
10.	Olive Stone Wooden Residue	<p>Specimens had satisfactory physico-mechanical properties by adding the waste up to 9%.</p> <p>Insulation properties improvement: YES <input checked="" type="checkbox"/>, NO <input type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Energy saving during sintering process: YES <input checked="" type="checkbox"/>, NO <input type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/>, NO <input checked="" type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/>, NO <input type="checkbox"/>, N/A <input checked="" type="checkbox"/></p>
11.	Oil refinery sludge	<p>Specimens had satisfactory physico-mechanical properties by adding the waste up to 5%.</p> <p>Insulation properties improvement: YES <input checked="" type="checkbox"/>, NO <input type="checkbox"/>, N/A <input type="checkbox"/></p> <p>Energy saving during sintering process: YES <input checked="" type="checkbox"/>, NO <input type="checkbox"/>, N/A <input type="checkbox"/></p>

		Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/> Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/>
12.	Carbon solid residue from the pyrolysis of used tyres	Specimens had satisfactory physico-mechanical properties by adding the waste up to 5%. Insulation properties improvement: YES <input checked="" type="checkbox"/> , NO <input type="checkbox"/> , N/A <input type="checkbox"/> Energy saving during sintering process: YES <input checked="" type="checkbox"/> , NO <input type="checkbox"/> , N/A <input type="checkbox"/> Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/> , NO <input type="checkbox"/> , N/A <input checked="" type="checkbox"/> Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/>
13.	Glass waste	Specimens had satisfactory physico-mechanical properties by adding the waste up to 7,5%. Insulation properties improvement: YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/> Energy saving during sintering process: YES <input type="checkbox"/> , NO <input type="checkbox"/> , N/A <input checked="" type="checkbox"/> Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/> , NO <input type="checkbox"/> , N/A <input checked="" type="checkbox"/> Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/> , NO <input type="checkbox"/> , N/A <input checked="" type="checkbox"/>
14.	Cement-asbestos wastes	Specimens had satisfactory physico-mechanical properties by adding the waste up to 10%. Insulation properties improvement: YES <input checked="" type="checkbox"/> , NO <input type="checkbox"/> , N/A <input type="checkbox"/> Energy saving during sintering process: YES <input type="checkbox"/> , NO <input type="checkbox"/> , N/A <input checked="" type="checkbox"/> Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input checked="" type="checkbox"/> , NO <input type="checkbox"/> , N/A <input checked="" type="checkbox"/> Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/> , NO <input type="checkbox"/> , N/A <input checked="" type="checkbox"/>
15.	Roof tiles waste	Specimens had satisfactory physico-mechanical properties by adding the waste up to 6%. Insulation properties improvement: YES <input checked="" type="checkbox"/> , NO <input type="checkbox"/> , N/A <input type="checkbox"/> Energy saving during sintering process: YES <input checked="" type="checkbox"/> , NO <input type="checkbox"/> , N/A <input type="checkbox"/> Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/> , NO <input type="checkbox"/> , N/A <input checked="" type="checkbox"/> Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/> , NO <input type="checkbox"/> , N/A <input checked="" type="checkbox"/>
16.	Aluminium electrostatic painting sludge	Specimens had satisfactory physico-mechanical properties by adding the waste up to 3%. Insulation properties improvement: YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/> Energy saving during sintering process: YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/> Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/> Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/>
17.	Alternative Solid Fuel (ASF)	Specimens had satisfactory physico-mechanical properties by adding the waste up to 6%. Insulation properties improvement: YES <input checked="" type="checkbox"/> , NO <input type="checkbox"/> , N/A <input type="checkbox"/> Energy saving during sintering process: YES <input checked="" type="checkbox"/> , NO <input type="checkbox"/> , N/A <input type="checkbox"/> Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/> Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/>
18.	Waste from sugar production industry + petcoke	Specimens had satisfactory physico-mechanical properties by adding the waste up to 5% for sugar industry waste & 5% for petcoke. Insulation properties improvement: YES <input checked="" type="checkbox"/> , NO <input type="checkbox"/> , N/A <input type="checkbox"/> Energy saving during sintering process: YES <input checked="" type="checkbox"/> , NO <input type="checkbox"/> , N/A <input type="checkbox"/> Air pollution from flue gases due to waste incorporation into the ceramic mass (law limits excess): YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/> Leachate pollution with heavy metals or other dangerous substances (law limits excess): YES <input type="checkbox"/> , NO <input checked="" type="checkbox"/> , N/A <input type="checkbox"/>

N/A means that the relevant measurements have not been done.

Properties evaluation was done by using prototype specimens (100% clay) that have been produced under the same conditions.