

## Use of OVH residue in the ceramics industry

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Este trabajo ha sido presentado como comunicación oral en el XI World Congress on Ceramic Tile Qualicer. (Castellón, España, 2010)

Hydrothermal oxidation (OVH: "Oxydation par Voie Humide") is an innovative technology used for waste water treatment, which is presented as an alternative to sewage sludge spreading and incineration. This process generates a fine-grain (D50 = 2  $\mu$ m) mineral by-product, which is very useful for the ceramics industry due to its high content in argillaceous elements, quartz, phosphate and calcium carbonate.

Therefore, this work describes the recycling of this OVH residue in the ceramics industry, and more particularly in the manufacture of calcareous earthenware wall tiles.

The residue can be combined with a white calcareous earthenware body up to a level of 7% without significant colorimetric deterioration, and if this is raised to 15%, it is possible to completely replace the crushed chalk, some of the quartz and reduce costly imported tight-burning clays by 6%. The developed body exceeds standardised requirements (modulus of rupture: + 40%; moisture swelling and glaze quality), which means that a 20°C reduction in firing temperature might be envisaged.

An industrial pilot test of 1500 kg conducted by the DESVRES site managers with 100 m<sup>2</sup> of tiles (format: 15 x 20 cm) confirmed these laboratory results, in particular validating the absence of rheological disturbance of the slip and the harmlessness of the addition on the maturing glaze quality. Furthermore, the nature of the fumes emitted in the test complied with current regulations, and the finished product did not exceed the thresholds defined by European regulations for inert waste classification.

*Keywords: Slurry re-use, Argillaceous Residue, Tiles Industry, Sustainable Development.*

### Utilización de residuos OVH en la industria cerámica

La oxidación hidrotérmica (OVH: "Oxydation par Voie Humide" u oxidación por vía húmeda) es una tecnología innovadora usada en la depuración de las aguas residuales, que se presenta como alternativa al esparcimiento y a la incineración de los lodos de aguas negras. Este proceso genera un producto derivado de mineral de grano fino (D50 = 2  $\mu$ m) que es muy útil para la industria cerámica debido a su elevado contenido en elementos arcillosos, cuarzo, fosfato, y carbonato de calcio.

Por tanto, este trabajo proporciona una descripción del proceso de reciclaje de este residuo de OVH en la industria cerámica, y más concretamente en la fabricación de azulejos de pasta calcárea.

Se puede combinar el residuo con una pasta de azulejo calcárea hasta un contenido del 7% sin que se produzca un deterioro colorimétrico significativo y, si se aumenta hasta el 15%, es posible sustituir por completo la caliza triturada, algo del cuarzo y, además, reducir el alto coste de las arcillas vitrificadas de importación en un 6%. El soporte desarrollado supera los requisitos de la normativa (modulo de ruptura: + 40%; dilatación por humedad y calidad del esmalte), lo que significa que se podría prever una reducción de 20°C en la temperatura de cocción.

Un ensayo piloto a nivel industrial, de 1500 kg, llevado a cabo por los gestores de las instalaciones de DESVRES con 100 m<sup>2</sup> de baldosas (formato: 15 x 20 cm) confirmó estos resultados de laboratorio, validando, en particular, la ausencia de una perturbación de la barbotina y la inocuidad del material incorporado en la calidad de maduración del esmalte. Además, la naturaleza de los gases emitidos durante el ensayo cumplió con la normativa vigente, y el producto acabado no sobrepasó los umbrales de tolerancia definidos por la Normativa Europea para la clasificación de los residuos inertes.

*Palabras clave: Aprovechamiento de la barbotina, Residuo Arcilloso, Industria Cerámica, Desarrollo Sostenible.*

## 1. INTRODUCTION

Faced with the difficulty of agricultural spreading of sewage sludge from waste water treatment plants, the VEOLIA Environnement group developed an original treatment for this sludge, which when pressurised to 250 bar in a pure oxygen atmosphere produces a mineral residue rich in argillaceous elements, quartz and calcium carbonate.

This by-product, which has a genuine asset in its natural fineness (D50: 2 $\mu$ m), has proven to be a real raw material for the ceramics industry, and more particularly in the production of calcareous earthenware wall tiles.

After a brief presentation of the ATHOS process (original waste water treatment process), the present article focuses on the study of the recycling of the residue conducted by SFC (Industrial Technical Centre for Ceramics) with the support of Soci t  Francaise de Ceramique, ADEME.

## 2. THE ATHOS PROCESS

The ATHOS process (Figure 1) uses the hydrothermal oxidation (OVH) principle, an oxidation operation in a liquid medium which consists in heating to a high temperature a pressurised effluent in the presence of an oxidising gas (air or oxygen) ([1], [2], [3] quoted in [4]). ATHOS is a concept combining hydrothermal oxidation with a biological treatment which mineralises the organic material in the sludge at a temperature of around 250°C at a pressure of 50 bar in a pure oxygen atmosphere. It generates 3 by-products:

- a gaseous discharge
- a biodegradable organic liquid
- a primarily mineral solid that we will refer to as "OVH residue"

The OVH residue emerges from the settling tank in the form of a highly liquid sludge, with a dry matter of around 6%. This sludge is then dehydrated by means of a filter press. At the end, a residue is obtained in the form of cakes with a dry matter of around 70%. For 1 tonne of sludge coming from the treatment plant, between 10 and 20 kg of OVH residue is obtained.

## 3. EXPERIMENTAL PART

### 3.1 Characterisation of OVH residue

Comprising 80% particles of less than 10  $\mu$ m (D50: 2  $\mu$ m), the OVH residue is similar to a wet argillaceous mineral ( $\approx$ 50% of dry extract) rich in limestone, quartz and phosphate (see Figure 2). Its fineness, as well as the presence of argillaceous elements such as smectite, gives it very good plastic and cohesive characteristics which are essential for ceramic shaping. It is however important to note a high ferric oxide content (around 4%), a ceramic colouring oxide.

Oxides	Residue %w
LOI	19.2
SiO <sub>2</sub>	31.5
Al <sub>2</sub> O <sub>3</sub>	7.4
TiO <sub>2</sub>	0.6
Fe <sub>2</sub> O <sub>3</sub>	3.7
CaO	22.8
MgO	1.4
K <sub>2</sub> O	1.0
Na <sub>2</sub> O	0.3
P <sub>2</sub> O <sub>3</sub>	7.1

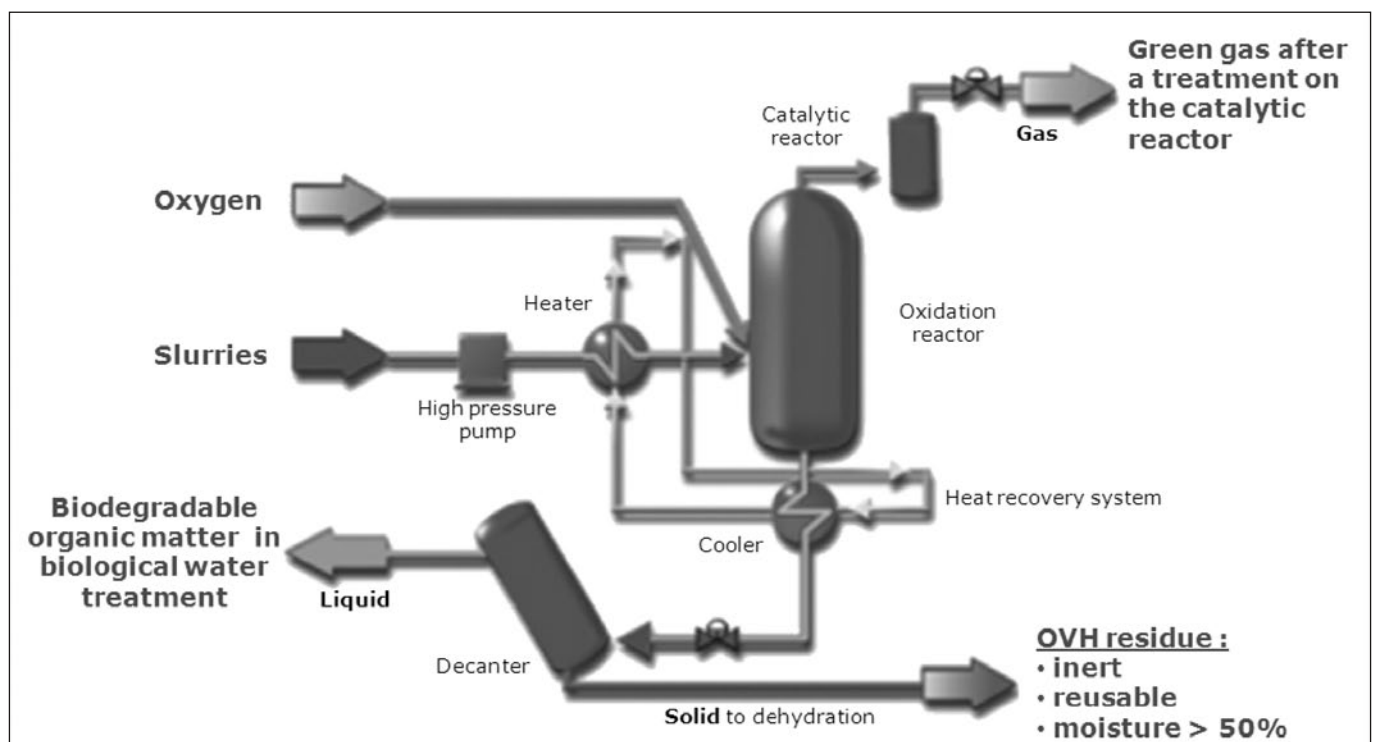


Figure 1. ATHOS process diagram

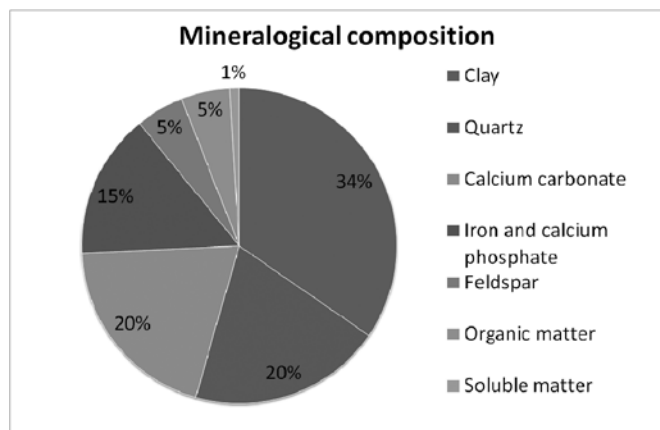


Figure 2. Chemical and mineralogical compositions of OVH residue

### 3.2 Test mixtures

Given the high calcium carbonate content and the characteristics presented above, this OVH residue was inserted into a white calcareous earthenware body for wall tiles, while maintaining the reference body composition. All of the chalk and some of the clays and quartz were eliminated in favour of 15% residue, supplying:

1. 6% argillaceous elements
2. 3% quartz
3. 6% chalk (i.e. 3.5% CaO)

At the SFC laboratory, the compositions above (Table 1) were prepared by means of a wet process:

After crushing the raw materials in a ball mill (Alsing), the slip obtained (d=1700 g/l; 3% remaining at 63 μm; Ø 4 mm Ford cup viscosity 18s) was enclosed in a plaster mould and then the past obtained was dried to a moisture level of around 10%.

Following FREWITT granulation to 1 mm (and controlled drying to a moisture level of below 6%), 100x100x5 mm format tiles were pressed under a pressure of 20 MPa.

TABLE I. TEST COMPOSITIONS

Raw materials	Composition (%)		
	Reference	TS 15	TS 7
Quantity produced	10 kg (SFC)	10 kg (SFC)	1.5 T (factory pilot)
Clays	49	43	46
Feldspar	24	24	24
Sand	12	9	11
Chalk	6	-	3
Miscellaneous	9	9	9
OVH residue	-	15	7
Total	100	100	100

After oven drying at 110°C, the tiles were fired in a gas cell at a temperature of 1100°C (heating 2000°C/h during 20 mins). Firing at a lower temperature was also carried out.

A pilot test on 1.5 t body was conducted with an addition level of 7%, due to the coloration of the white body in the laboratory when 15% was added (coloration due to the presence of iron oxide; see Figure 2).

Besides the difference in scale, the process differed in the atomisation of the slip produced; as well as in a shorter firing cycle: body fired at 1150°C over 35 mins + glaze fired at 1110°C over 31 mins.

Tiles measuring 150x200 mm made in the factory were glazed in order to check the harmony between the glaze and the body.

Tiles made in this way were characterised with current standards:

1. Firing shrinkage
2. Colour L\*a\*b\*
3. Flexural strength
4. Porous texture (water absorption PEA + bulk density DA)
5. Moisture swelling

## 4. RESULTS AND DISCUSSION

### 4.1 Laboratory Test

The results obtained at laboratory were detailed at tables I, II and III.

TABLE II. LABORATORY SCALE TEST RESULTS

	Laboratory scale			
	Reference	TS15		
Firing temperature	1100°C	1100°C	1080°C	
Firing shrinkage (%)	0.1	1.8	1.1	
Porous texture	PEA (%)	15.4	14.5	15.9
	DA	1.88	1.9	1.86
Flexural strength (MPa)	12	17	14	
Colour of body	L*	86	66	69
	a*	4	17	16
	b*	15	28	26
Moisture swelling (mm/m)	0.41	0.28	0.32	

Adding 15% OVH residue to the calcareous earthenware body results in the development of a more coloured material (orange-red), which is less porous and stronger (see Figure 3 and Table 3).

The high reactivity of the OVH residue is therefore revealed by the development of a denser tile, which has greater shrinkage, but improved mechanical properties.

These results obtained at 1100°C led us to reduce the firing temperature of the body by 20°C (to 1080°C) in order to obtain a texture comparable to the reference, while retaining a mechanical improvement.



Figure 3. Appearance of non-glazed tiles (Ref. TS7 and TS15)

NB: Note that the development of a pink colour, disadvantageous in French calcareous earthenware bodies (which are white), does not appear to be a problem for the production of Spanish (and Italian) red body tiles.

#### 4.2 Industrial scale

TABLE III. INDUSTRIAL SCALE TEST RESULTS

		Industrial scale	
		Reference	TS7
Firing shrinkage (%)		0.2	0.6
Porous texture	PEA (%)	19.0	17,1
	DA	/	/
Flexural strength (MPa)		12	16
Colour of body	L*	87	82
	a*	2	5
	b*	11	15
Moisture swelling (mm/m)		0.37	0.28

The improvements observed in the laboratory were confirmed on an industrial scale (mechanical strength, bulk density...), even with the addition level reduced to 7%.

Furthermore, this reduction was able to minimise the colorimetric impact due to the presence of ferric elements (see Figure 3).

The developed surface enamel proved to be a good match, and the absence of flaws (such as glaze pinholes) attested to the good compatibility of the residue.



Figure 4. Firing of tiles (200x150 mm) in an industrial kiln

#### 4.3 Analysis of fumes

The fumes extracted from the kiln during industrial firing of the tiles were analysed by means of a Fourier transform infrared spectroscopy (FTIR): monitoring the gases  $N_2O$ ,  $NO$ ,  $NO_2$ ,  $NH_3$ ,  $SO_2$ ,  $HCl$ ,  $HF$ ,  $H_2O$ ,  $CO_2$ ,  $CH_4$ ,  $CO$ ,  $O_2$ .

During firing, some concentration gases of the body increased with the addition of OVH residue to the kiln ( $CH_4$ ,  $NH_3$  and  $NO_x$ ); however, these increases were not significant and the concentrations measured were still below the values set by Prefectural Order, and by the European Directive on waste incineration from December 2<sup>nd</sup> 2000. See table IV.

#### 4.4 Environmental impact

Glazed tiles with and without residues were subjected to leaching tests as per standard NF EN 12457-2 in order to evaluate the environmental impact of adding OVH residue. These tests demonstrate that tiles with 7% OVH residue are similar to inert waste according to the 2006/03/15 Order which establishes the list of products permissible in inert waste storage facilities.

### 4.5 Industrial report

The possibility and benefit of using an OVH residue in earthenware bodies were therefore confirmed on an industrial scale with the manufacture of 1.5 t of 150x200 mm tiles of superior quality. The absence of rheological disturbance, environmental impacts (fumes and leaching from tiles) and the harmlessness of the addition on the glaze maturing quality give this material the profile of a real eco-friendly product for the ceramics industry.

### 5. CONCLUSION

- As this study shows, the incorporation of OVH residue in the ceramics industry is possible.
- The OVH residue studied proved to be a good candidate as a raw material for the ceramics industry, and in particular in production of calcareous earthenware wall tiles.
- Its composition, combined with its natural fineness (an undeniable advantage for the crushing cost) ensures a significant 7% reduction of more or less costly raw materials (quartz, clays, chalk), without significant colorimetric deterioration; a reduction which can be increased to 15% in the case studied with slight coloration of the body.
- The high reactivity of this product leads to a densification of the product, with an increased mechanical strength, which should make possible a reduction of the firing temperature by around 20°C.

- VEOLIA manufacturers and operators are very keen for every sludge treatment plants equipped with an OVH became a production site for a by-product with sufficient chemical stability to be incorporated into modern tile production.

TABLE IV. FAME ANALYSIS

Gases	REF (mg/Nm <sup>3</sup> )	TS7 (mg/Nm <sup>3</sup> )	Limit* (mg/Nm <sup>3</sup> )
HCl	≈10		10
HF	≈25		50**
SO <sub>2</sub>	≈15		50
NO <sub>2</sub>	≈15		200
N <sub>2</sub> O	1	5	200
NH <sub>3</sub>	1	15	/
CH <sub>4</sub>	3	8	/

\* as per the European Directive on waste incineration  
 \*\* as per Prefectural Order

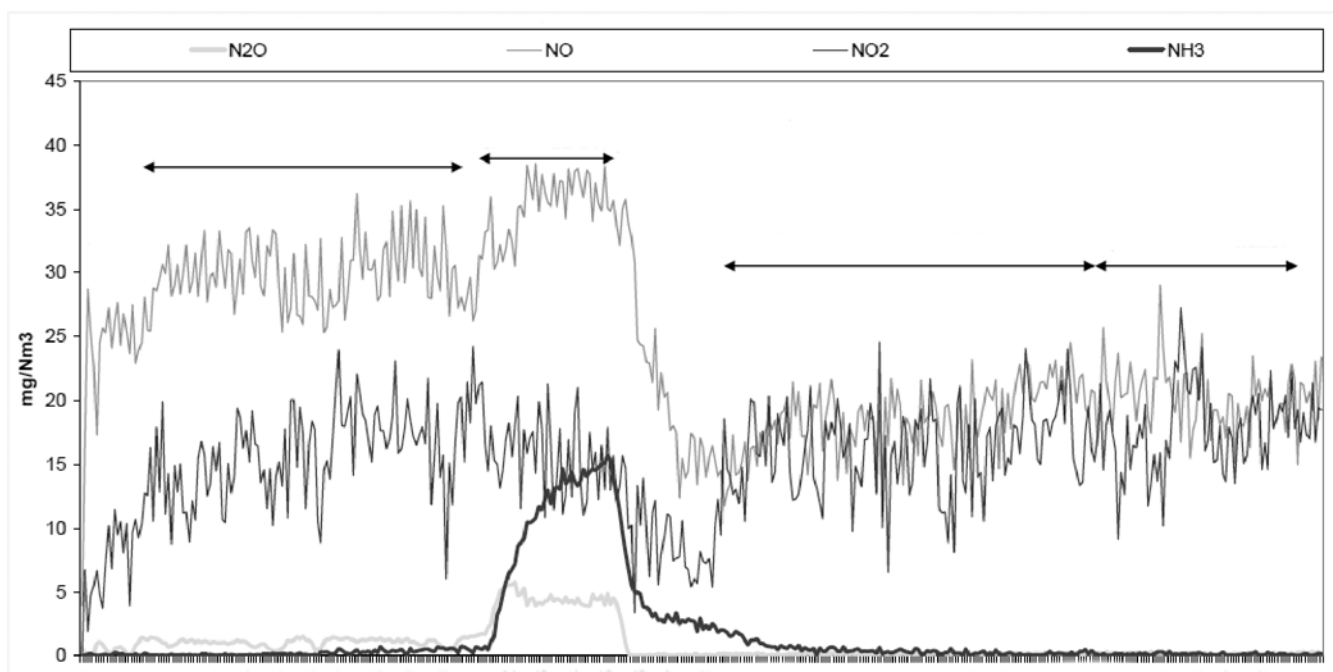


Figure 5. Emission of gases during Industrial firing

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Recibido: 6-5-10

Aceptado: 13-7-10

