MICROPOLLUTANTS IN AN ITALIAN KAOLIN: ASSESSMENT AND FORMATION PROPOSAL

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Introduction

Kaolinitic rocks can be originated in 2 different ways: from the action of volcanic fluids that altered some feldspar containing rocks, the so called primary Kaolin and secondary, showing a sedimentary formation after the weathering, erosion and transport of the primary rocks. Typical of the latter are the "ball clays", also called "plastic clays", that are used as main raw material in ceramics as they keep a white color after "cooking" as well as animal feed ingredients as binder and anticaking additives. Primary Kaolin, that is mainly constituted by kaolinite clay, is used in a wide amount of applications like in pottery (also in bone china if mixed with bone powder), in pharmaceutical industry as excipients and in paper industry.

In the past years PCDD/Fs contained in the above rocks created serious contamination problems in different part of the world[1,2,3,4]. The PCDD/Fs source has been certainly recognized as non anthropogenic from their "natural pattern" but their formation model has not been uniformly accepted[5,6].

Recent data reported from the Italian Society of Ceramics[7] shows that in Italy there are 4 mines for secondary kaolin, producing 1,000,000 tonnes/year and only one mine for "primary" kaolin producing 500,000 tonnes/year. This mine in located in Monte Sughereto, Sasso di Furbara, Rome Province. The aim of the present study was to assess the presence of organic micropollutants in the kaolinic ore and try to better understand the kaolin and micropollutants origin.

Materials and methods

Samples

Kaolin extraction method is based on the selective mining of the visually enriched part of the mine. The "Run of Mine" (ROM) is separated into 3 different fractions by color, depending on the different iron contents that do generate a decrease in economic value with the iron increase, then generate the feed of closed circuit composed by a jaw crusher-sieve-mill: oversize sieve (+7 mm) feeds the mill, while undersize sieve (-7mm), that constitutes our samples, feeds the enrichment plant. Kaolin is enriched by means of attrition cells and water flow that simply separates the main ore from the gangue. One sample of the gangue, mainly constituted by quartz, was also taken.

Chemical Analysis

The chemical composition of the sample was performed by XRF (Pioneer S4, Bruker AXS), kindly provided by the mine property (Minerali Industriali SpA) and shown on Table 1.

Size distribution

Samples have been first wet sieved. Then, the -500 μm fraction has overcome the laser diffraction particle analysis (Bettersize, China. Model BT-2003, with range lens 0,040-0,600 mm). Results are shown in Table 2 and figure 1

Table 1 – Sample chemical composition by XRF

Sample name	MgO %	Na2O %	Fe2O3 %	TiO2 %	SiO2 %	CaO %	K2O %	Al2O3 %	P.F. %	CO2 %	S %
Kaolin BGS 07	0,1	0,23	0,72	0,21	78,9	0,05	0,43	14,17	5,13	0,3	0,24
Kaolin BGS 01/10	0,03	0,17	0,22	0,16	77,8	0,05	0,23	15,43	5,87	0,23	0,33
Kaolin BG	0,07	0,11	1,49	0,12	77,9	0,05	0,15	14,6	5,43	0,21	0,23
Silica Gangue SG	0,04	0,11	1,18	0,04	85	0,03	0,19	9,7	3,54	0,12	0,12

Table 2– Sample oversize percent after wet sieved

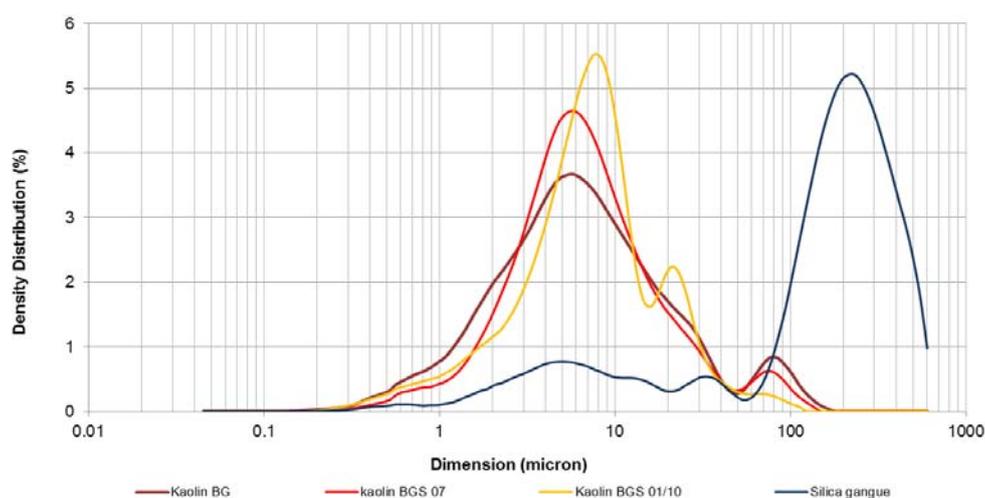| Dimension (mm)	Silica Gangue SG %	Kaolin BGS 01/10 %	Kaolin BGS 07 %	Kaolin BG %
+ 4	23,11	28,02	39,51	26.02
- 4 + 2	34,07	12,10	14,71	13.53
- 2+ 1	22,58	9,75	8,40	8.49
-1+0.5	5,18	7,40	5,87	5.00
-0.5	15,06	42,74	31,51	46.95

Figure 1. – 0,5mm particle size distribution (Bettersize Model BT-2003). It is possible to see 2 particle size populations: the finer the kaolin, the bigger the silica.

Automated clean-up

The samples were ground and dried at 50 ° C for 48 hours and 30 g sample was spiked with EPA1613-LCS (Wellington Laboratories) extracted by Accelerated Solvent Extractor (Dionex ASE 200) using toluene. The extract was evaporated to 1 ml using a Rotavapor (Büchi) and then a stream of nitrogen evaporator set at 40 ° C. The samples were brought to 5 ml with methylene chloride and then purified with an automated system based on size exclusion chromatography and described elsewhere[8]. The automated clean-up system (Accuprep J2 Scientific) consists of a 2.5 cm x 45 cm glass column packed with BioBeads SX-3 resin in 100% methylene chloride, a pump, an auto sampler and an in line evaporating chamber. The whole system is computer controlled and can be programmed as required (i.e. volume, flow-rates, direction of solvent flow, etc.). The system used a 5-mL sample loop and a flow rate of 5 mL/min with methylene chloride as the mobile phase. Briefly, the sample is loaded on the GPC column and after the elution, is concentrated in the AccuVap module up to a final volume of 0.5 ml. Then it is loaded on the SPE alumina column and the collected fraction is sent again to the AccuVap module, where it is concentrated up to a volume of 1.5 ml. The sample is manually dried under a gentle stream of nitrogen and after addition of PCDD $^{13}C_{12}$-labelled internal standards (EPA1613-IS , Wellington Laboratories) the samples were analyzed.

Analysis

Purified extracts were analysed by a Trace GC Ultra high resolution gas chromatograph equipped with an TriPlus autosampler and coupled by a heated transfer line to an TSQ Quantum Triple Quadrupole GC-MS/MS spectrometer (Thermo Scientific). Chromatographic separation was achieved with a GsBP (GS-Tek) fused-silica capillary column (60 m x 0.25 mm ID, 0.25 μm film thickness) with helium as carrier gas in Splitless injection mode.

Results

The analytical results are shown in Table 3. (Values above LOD are highlighted in grey). They have to be reviewed according to the new ore deposit minero-genetic model described below.

Table 3 – PCDD/F content for the four samples analysed

	Kaolin BGS01/10		Kaolin BGS/07		Kaolin BG		Silica Gangue	
	(pg/g)	TEQ (pg/g)	(pg/g)	TEQ (pg/g)	(pg/g)	TEQ (pg/g)	(pg/g)	TEQ (pg/g)
2,3,7,8-TetraCDD	< 0,017	< 0,0167	< 0,017	< 0,0167	< 0,017	< 0,0167	< 0,017	< 0,0167
1,2,3,7,8-PentaCDD	< 0,083	< 0,0417	< 0,083	< 0,0417	< 0,083	< 0,0417	< 0,083	< 0,0417
1,2,3,4,7,8-HexaCDD	< 0,083	< 0,0083	< 0,083	< 0,0083	< 0,083	< 0,0083	< 0,083	< 0,0083
1,2,3,6,7,8-HexaCDD	< 0,083	< 0,0083	< 0,083	< 0,0083	0,1862	0,0186	< 0,083	< 0,0083
1,2,3,7,8,9Hexa-CDD	< 0,083	< 0,0083	< 0,083	< 0,0083	0,2172	0,0217	0,2914	0,0291
1,2,3,4,6,7,8-HeptaCDD	< 0,083	< 0,0008	0,9615	0,0096	0,9823	0,0098	3,4625	0,0346
OctaCDD	0,6959	0,0007	7,5945	0,0076	7,3080	0,0073	33,6990	0,0337
2,3,7,8-Tetra CDF	< 0,017	< 0,0017	< 0,017	< 0,0017	< 0,017	< 0,0017	< 0,017	< 0,0017
1,2,3,7,8-PentaCDF	< 0,083	< 0,0042	< 0,083	< 0,0042	< 0,083	< 0,0042	< 0,083	< 0,0042
2,3,4,7,8-Penta CDF	< 0,083	< 0,0417	< 0,083	< 0,0417	< 0,083	< 0,0417	< 0,083	< 0,0417
1,2,3,4,7,8-HexaCDF	< 0,083	< 0,0083	< 0,083	< 0,0083	< 0,083	< 0,0083	< 0,083	< 0,0083
1,2,3,6,7,8-HexaCDF	< 0,083	< 0,0083	< 0,083	< 0,0083	< 0,083	< 0,0083	< 0,083	< 0,0083
2,3,4,6,7,8-HexaCDF	< 0,083	< 0,0083	< 0,083	< 0,0083	< 0,083	< 0,0083	< 0,083	< 0,0083
1,2,3,7,8,9-HexaCDF	< 0,083	< 0,0083	< 0,083	< 0,0083	< 0,083	< 0,0083	< 0,083	< 0,0083
1,2,3,4,6,7,8-HeptaCDF	< 0,083	< 0,0008	< 0,083	< 0,0008	< 0,083	< 0,0008	< 0,083	< 0,0008
1,2,3,4,7,8,9-HeptaCDF	< 0,083	< 0,0008	< 0,083	< 0,0008	< 0,083	< 0,0008	< 0,083	< 0,0008
OctaCDF	< 0,167	< 0,0002	< 0,167	< 0,0002	< 0,167	< 0,0002	< 0,167	< 0,0002
PCDD/PCDF	**1,9793**	**0,1675**	**9,7560**	**0,1832**	**9,7271**	**0,2068**	**38,5696**	**0,2551**

Discussion

The model[9] for the minerogenesis of the Monte Sughereto kaolin deposit indicates three main phases. During the initial two phases the deposition of diffused Fe and As sulphides occurred due to the ascent of mineralizing fluids linked to the final stages of the volcanic dome emplacement. During the third most important phase, the dissolution of the previously deposed Fe-sulphides under oxidizing conditions took place, with the formation of acid solutions. The massive alteration of the unaltered rock resulted at this stage. The occurrence of silicified and kaolinitized products through the outcrop is interpreted as due to local variation of pH conditions. The alteration process took place via a strong depletion of alkali, alkali-earth and metallic (Fe) elements, with resulting passive enrichment of silica and alumina. Therefore, Monte Sughereto kaolin ore deposit should be considered as a secondary deposit and its micropollutants contents it is very low.
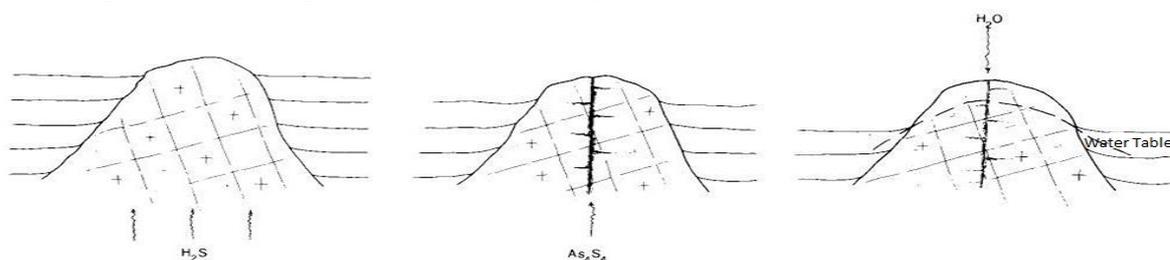

Figure 2 – Monte Sughereto minerogenetic model modified by Barrese et al.[5]

There are several hypothesis on PCDDs presence in kaolin: some authors indicate an anthropogenic origin whereas others suggest a natural origin. The second hypothesis is strongly supported, for example, by studies on carbon isotope composition of OCDD in ball clays from the U.S. and Japan[10]. It was also confirmed from another work[11] showing that under laboratory conditions, microorganisms like "Phanerochaete chrysosporium" were able to produce chlorphenols, precursor of PCDDs, by degradation of lignite. From chlorphenols condensation PCDDs are obtained but whether the enzymatic reactions leading to the complete chlorination of PeCP and then through the loss -2H with formation of Phenoxyphenol (POP) and subsequent loss of 2 Cl [12], only the OCDD will be obtained. Obviously, the amount of formed OCDD depends on the amount of lignite in the soil. For this reason, literature shows that the highest concentrations of dioxins are present in lignitic clays. For example it was found[13] a PCDD concentration of 3-91 pg/g in primary kaolin, 711-45935 pg/g in secondary kaolinitic clay and 13513-1191120 pg/g in lignitic clays. Although the samples analyzed in this work are of secondary kaolin samples and, as reported in literature data, they contain almost no PCDFs, the range of OCDDs found (0.7-33 pg/g) is typical of primary kaolin. Other authors[14] provided the evidence about clay-catalyzed OCDD formation. They mixed Fe(III)-montmorillonite with pentachlorophenol under ambient temperature in the presence of water. After minutes up to days approximately 5 mg OCDD/kg clay were formed. This study is a remarkable indication of the proposed hypothesis of in situ formation of OCDD in soils. During the analysis of our samples we noted that in two samples of kaolin with comparable amounts of iron there is a similar quantity of OCDD while in the sample with the least amount of iron there is much lower OCDD. In the Silica Gangue sample, which has a different ratio silica/alumina, there is an even higher concentration of OCDD, although there is an amount of iron comparable to the first two samples. Probably comes into play the different capacity of silica and alumina to seize OCDD precursors.

Acknowledgements

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