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Method of inerting mineral residues

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The present invention relates to a method of inerting mineral residues. More particularly, it relates to a method of inerting automobile grinding residues.

The expression « inerting a residue » is understood to mean a treatment after which the toxic substances that the residue contains are immobilized therein and no longer present a risk of contaminating the environment.

The ever increasing quantities of scrapped motor vehicles (SMVs) pose serious problems as regards the removal of the residues that result therefrom.

National legislation imposes substantial levels of recovery and recycling of the constituent materials of motor vehicles. To meet these requirements, it is common practice for the motor vehicles to be ground up, so as to allow the metals, mainly ferrous metals, to be separated and recovered. However, the residues that remain after this recovery, commonly called AGRs (automobile grinding residues), still represent about 25% of the weight of the original vehicle. These residues comprise organic, often toxic, substances and heavy metals. These toxic substances are liable to contaminate the environment, in particular by being leached, if they are not sufficiently immobilized in the residue.

There are various standardized tests that any residue must pass for the purpose of utilizing it or even for dumping it.

Automobile grinding residues do not in general pass these tests. In particular, the quantities of chromium(VI) and lead that are detectable in leachates greatly exceed the imposed standards. These residues must therefore undergo a prior inerting treatment.

A known method for inerting automobile grinding residues consists in subjecting them to a vitrification heat treatment carried out at high temperature, of around 1300°C.

However, this known method has the disadvantage of volatilizing a substantial portion of the heavy metals contained in the treated residue. It is consequently necessary to purify the flue gases resulting from the said treatment. Moreover, the high temperatures used in this known treatment mean that a large amount of energy is consumed.

The invention aims to remedy the aforementioned drawbacks by providing a simple and inexpensive method of inerting automobile grinding residues that makes these residues innocuous so as to allow them to be utilized or dumped.

Consequently, the invention relates to a method of inerting mineral residues comprising automobile grinding residues, in which method water is added to the mineral residues so as to form a paste, the paste is mixed with phosphoric acid, and the resulting mixture undergoes a calcination operation.

According to the invention, the mineral residues comprise automobile grinding residues. In general, they comprise more than 35% by weight, often more than 50%, thereof. They may also comprise residues from domestic electrical appliances, such as refrigerators and cookers, these also being ground. Finally, the mineral residues may comprise residues coming from various collection points, for example those resulting from the demolition of buildings.

The mineral residues subjected to the treatment according to the invention are composed of fragments, generally with a particle size of less than 5 mm. However, certain fragments of the fibrous type do have a length that sometimes reaches 10 mm, but the mean particle size is less than 5 mm.

In an advantageous way of implementing the method according to the invention, the mineral residues are ground in such a way that their mean particle size is less than 2 mm, preferably between 0.5 and 1.5 mm.

The fragments are highly heterogeneous, namely metal fragments and fragments of glass, plastic, wood, textile, etc., the whole assembly being embedded in an indistinct mass that contains hydrocarbons. The hydrocarbon content of the mineral residues is usually between 10 and 20% by weight. The bulk density of the residue is ordinarily less than 1. The water content of the residue, determined by volumetry using the Karl Fischer method, is generally between 3 and 5%.

The mineral residues subjected to the inerting according to the invention contain little calcium carbonate. This content is generally less than 6% by weight. Frequently, the calcium carbonate content of the mineral residues is less than 4%. However, it is preferably greater than 1%.

The mineral residues subjected to the method according to the invention contain heavy metals. The term « heavy metals » is understood to mean metals whose density is at least equal to $5 g/cm^3$, and also beryllium, arsenic, selenium and antimony, in accordance with the generally accepted definition (Heavy

Metals in Wastewater and Sludge Treatment Processes ; Vol I, CRC Press Inc, 1987; p.2).

According to the invention, water is added to the mineral residues in order to convert them into a paste. The word « paste » is understood here in the rheological sense, denoting a viscous liquid. The amount of water to be added depends on the initial water content of the residue. It is advantageous to add an amount of water such that the paste obtained contains between 20 and 50% by weight of water, which in the majority of cases corresponds to an addition of 15 to 47% by weight of water.

The paste obtained is then mixed with phosphoric acid. It is very suitable for the amount of phosphoric acid to be between 5 and 20% by weight of the mineral residues to be treated. However, this amount is preferably greater than 7%, but advantageously less than 15%. The water and the phosphoric acid are added with stirring. Any stirring and mixing technique can be used. Plough mixers or the use of an endless screw give good results.

The resulting mixture is subjected to a calcination operation. The calcination is carried out at a temperature above 500°C for a time sufficient for the organic materials to be correctly destroyed. Advantageously, the calcination temperature remains below 1000°C, in order to prevent the volatilization of heavy metals.

In a first preferred way of implementing the method according to the invention, the calcination temperature is between 630 and 680°C. This method of implementation provides a treated residue that retains a pulverulent texture.

In a second preferred way of implementing the method according to the invention, the calcination temperature is between 730 and 780°C. In this method of implementation, the texture of the residue is more massive, but it remains friable.

In a third preferred way of implementing the method according to the invention, the calcination temperature is between 830 and 900°C. In this method of implementation, a treated residue is obtained that is partly vitrified and has good mechanical strength.

In certain cases and for certain applications, it may prove worthwhile to add a hydraulic binder to the treated residue and, where appropriate, water, in order to cause the binder to set. The final product obtained may then have remarkable mechanical properties.

Surprisingly, it has been observed that the mineral residues comprising automobile grinding residues, despite their low calcium carbonate content, give rise, during the calcination, to the formation of calcium pyrophosphate. Without wishing to be held by any theoretical explanation, the inventor believes that this calcium pyrophosphate is a heavy-metal trap.

The examples described below will bring out the benefit of the invention.

First series of trials

This series of trials started with what are called "heavy" grinding residues. These are residues collected directly downstream of the grinder.

Example 1 (not according to the invention)

Mineral residues having the following composition were treated :

Element	**% by weight**
Cd	0.0026
Cr	0.06
Cu	0.54
Fe	10.3
Ni	0.11
Pb	0.73
Zn	1.8
$CaCO_3$	3.1

The mineral residues were mixed with 20% water by means of an endless screw at room temperature and then calcined for 2 hours at 620°C, starting with a cold furnace, with a forced circulation of air.

The resulting product was subjected to the triple leaching test described in French Standard NFX 31 - 210. The test protocol consists in grinding the material so that it can pass through a 4 mm screen. This ground material is subjected to triple leaching with demineralized water, in a liquid/solid ratio of 10, with constant stirring. After each leaching, the heavy-metal content of the liquid for washing the powder subjected to the test is measured.

The results obtained were the following :

1st Leaching			2nd Leaching			3rd Leaching		
pH	Cr (VI) (mg/l)	Pb (mg/l)	pH	Cr (VI) (mg/l)	Pb (mg/l)	pH	Cr (VI) (mg/l)	Pb (mg/l)
11.6	3.9	16	11.2	1.0	< 0.03	11.0	1.7	< 0.03

Example 2 (according to the invention)

The procedure was as in the previous example except that 10% phosphoric acid was mixed with the residue, also by means of an endless screw, before its calcination.

The results of the leaching test were the following :

1st Leaching			2nd Leaching			3rd Leaching		
pH	Cr (VI) (mg/l)	Pb (mg/l)	pH	Cr (VI) (mg/l)	Pb (mg/l)	pH	Cr (VI) (mg/l)	Pb (mg/l)
9.3	0.08	< 0.03	10.1	< 0.002	< 0.03	9.9	< 0.002	< 0.03

Second series of trials

This series of trials started with what are called « light » grinding residues. These residues are collected indirectly, in the form of « dust » emitted into the atmosphere during the grinding operation.

Example 3 (according to the invention)

The procedure was as in the previous example, except that the calcination was carried out at 875°C and the initial composition of the residue to be treated was as follows :

Element	% by weight
Cd	0.003
Cr	0.065
Cu	0.47
Fe	(not measured)
Ni	0.07
Pb	1.41
Zn	2.2

The results of the leaching test were the following :

1st Leaching			2nd Leaching			3rd Leaching		
pH	Cr (VI) (mg/l)	Pb (mg/l)	pH	Cr (VI) (mg/l)	Pb (mg/l)	pH	Cr (VI) (mg/l)	Pb (mg/l)
11.3	< 0.002	< 0.03	10.8	< 0.002	< 0.03	10.9	< 0.002	< 0.03

These examples illustrate the surprising inerting effect obtained by the method according to the invention, despite the very low calcium carbonate content of the mineral residue.

CLAIMS

1 – Method of inerting mineral residues comprising automobile grinding residues, in which method water is added to the mineral residues so as to form a paste, the paste is mixed with phosphoric acid, and the resulting mixture undergoes a calcination operation.

2 – Method according to the preceding claim, characterized in that the mean particle size of the mineral residues is between 0.5 and 1.5 mm.

3 – Method according to either of the preceding claims, characterized in that the amount of phosphoric acid mixed is between 5 and 20%.

4 – Method according to the preceding claim, characterized in that the amount of phosphoric acid mixed is between 7 and 15%.

5 – Method according to any one of the preceding claims, characterized in that the calcination is carried out at a temperature of between 630 and 680°C.

6 - Method according to any one of Claims 1 to 4, characterized in that the calcination is carried out at a temperature of between 730 and 780°C.

7 - Method according to any one of Claims 1 to 4, characterized in that the calcination is carried out at a temperature of between 830 and 900°C.