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Reduction of pollutants in painting operation and suggestion of an optimal technique for extracting titanium dioxide from paint sludge in car manufacturing industries—case study (SAIPA)

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Abstract

Paint sludge of car manufacturing industries are not disposed in landfills, since they contain hazardous materials with a high concentration of chromium, aluminum, titanium, barium, copper, Iron, magnesium, strontium, and so on. Thus, it is essential to find solutions in order to neutralize them or suggest cost-effective techniques, which are also environmentally acceptable. Because, this sludge contains considerable amounts of Ti pigments and unbaked resins, recycling these pigments—which could be used in a variety of industries such as paint factories— is an appropriate subject for further research. In this article, with the aim of identification of main pollutants in order to eliminate them and suggest a cost-effective solution to recover the sludge, a large number of tests including X-ray fluorescence spectroscopy, X ray diffraction spectroscopy, and diffusion thermal analysis are conducted to determine types and concentration of elements, and combinations of paint sludge in car manufacturing industries. As titanium dioxide (TiO_2) is widely used as the main pigment of automobile paints, an optimal technique is suggested for extracting TiO_2 with high purity percentage through adopting scientific methods such as membrane and electrolysis.

Keywords

Car manufacturing industries, paint sludge, extraction, titanium dioxide

Introduction

Paint sludge containing polymeric resins, pigments, chemicals, organic solvents, and most importantly heavy metals and hazardous materials can result in soil and water (surface and ground water) contamination (Dabiri, 2006). The best way to solve these problems is the use of processes, which can produce valuable materials as well as reduce the load of pollution. Because titanium (Ti) is a strategic element, and its price and percentage are higher compared to other heavy metals in this sludge, research on extracting this substance is of a particular priority. A great deal of research had been carried out by leading companies such as Caterpillar, General Motors, Chrysler, Benz, Toyota, and so on, about the usage and recycling of paint sludge to strengthen metals and polymers, make construction materials such as cement and concrete, produce insulations and seals, and recover paint from the sludge (Chemical success story, 2001; Daimler, 1999, 2002; Environmental Services Division State of Michigan, 1994; www.toyotageorgetown.com).

In 1992, Weinwurm applied heating and calcinations of sludge in order to use it as a filling insulation (FUJI Heavy Industries (SUBARU), 2007).

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In 1999, experts in ASTER Company proposed a process for paint sludge used for making polymeric combinations for insulations, adhesives, plastics, and similar products. In subsequent years, Japanese Institute of Global Energy, and in 2002, researchers of Michigan University and Geracen et al. used paint sludge in plastic insulations, but recycling Ti and paint from car paint sludge requires further research (Gerace and Gerace, 1992; Gerace et al., 1999a, 1999b).

In this article, methods of extracting titanium dioxide (TiO_2) from paint sludge of car manufacturing and optimal use of such combinations are discussed. Accordingly, SAIPA Company was selected as a case study. At first, elemental and combinational analyses of paint sludge was carried out to identify types and amounts of elements within paint sludge of base water, then environment- friendly techniques were recommended of extracting Ti_2O.

Materials and methods

To conduct the test, paint sludge produced in painting, saloon no. 2 (the new painting saloon) was used. Samples were taken from paint sludge during two phases of storage tank. The purpose of first phase of sampling was elemental and combinational identification and analysis of paint sludge. In the second phase, sampling was carried out for extracting Ti_2O from paint sludge. And the following methods were employed in order to study existing combinations in paint sludge of the first phase and processes of Ti_2O extraction.

X-ray fluorescence spectroscopy (XRF). XRF is widely used in qualitative and quantitative analysis in various fields such as environmental, geological, industrial, and so on. It has advantages over other techniques such as atomic absorption spectroscopy (ASS), inductively coupled plasma spectroscopy (ICPS), and neutron activation analysis (NAA), including being non-destructive, multiplicity of elements, and having desirable speed and economic value. In this experiment, the solid samples should be burnished so that the surface becomes fully homogenous. For this purpose, paint sludge, which—in the form of clot—is removed from the solution of water and paint cascade (in SAIPA painting saloon) and the aqueous paint sludge was dried in an oven at 100°C (at this temperature, various combinations of elements undergo the least changes and the particular reaction which changes the combinations of the material does not occur; Wcaslab website). After the sample was dried, powdering was done by a pounder and XRF was conducted in order to identify and make a combinational analysis, estimate the amounts of these elements in paint sludge samples heated up to 1400°C, as well as find purity degree of suspension phase at the surface of water (Amptek website, 2002).

X-ray diffraction spectroscopy (XRD). XRD is an appropriate method for qualitative and quantitative studies on solid or liquid crystalline materials. The basis of this method is the diffraction of X-rays from atomic sheets with equal distance from each other and in compliance with Bragg's law. The amount of samples for each analysis determined to range from 0.5 to 3, depending on the type of sample, and lam technique or tablet making was used. The final results are presented in a quantitative form. To conduct this experiment, dried sample and powder (fine mesh) were used (Bhadeshia, 1996).

Diffraction temperature analysis (DTA). After the types of existing combination within paint sludge were analysed, DTA test was carried out in order to identify the reactions and the number of permutations that occurred as a result of heating. Sample preparation for DTA apparatus was performed as in XRD and XRF and the sample was made into powder and fully dried. Analysis of paint sludge sample was done by DTA apparatus in temperatures of up to 1200°C and a heating rate of 20°C. At 100°C, existing combinations in paint sludge were identified and heating continued until the temperature reached 1200°C in order to create baseline information to be used in future studies (Bhadeshia, 2004).

Inductively coupled plasma (ICP). ICP apparatus is an elemental analysis system, in which spectroscopy is diffusive and its atomization is carried through plasma. Plasma is a set of electrons and positive ions of high-energy Argon at 10,000K. This environment is created by means of high-energy radio waves. By producing a magnetic field, electrons and ions of plasma are circulated within a magnetic environment at far high velocity (Douglas, 2003). Neutral atoms of Argon are ionized in plasma due to collision with charged particles, leading to survival of the plasma. Neutral atoms of Argon are ionized in plasma due to collision with charged particles, leading to survival of the plasma. The sample is diffused through a thin sucking duct by means of Argon current in plasma ions are conveyed to the sample and it results in its atomization and excitation. Thus, the beams with particular wavelengths of elements existing in the solution are emitted, the location and the intensity of which show the type of element and amounts of the element, respectively. The precision of measurement is in parts per billion (ppb) level. To perform this experiment, the sample should be in the form of a solution (Douglas, 2010).

Membrane. According to definition, "membrane" is a thin layer by which parts of a fluid can be segregated selectively. In other words, membrane is a means, which allows for segregation of substances based on their molecular sizes. Therefore, it is essential that before using the membrane, scanning electron microscope (SEM) test should be carried out on the sample in question to find the size of the particles in paint sludge powder. In this research, ultra filtration (UF) membrane is used for segregation. To conduct the test, the dried and powdered sample reaches to the volume of 100cc by distilled water and is passed through the membrane (Madaeni, 2002, Madaeni and Rahimpour, 2005).

SEM. With the aid of SEM, this apparatus takes images of the surface with a magnification of 10–100,000 and a resolution of 3–100 nm (depending on the sample). Polishing techniques and standard H metallography are sufficient for conductors. Nonconductors are usually coated with a thin layer of carbon, gold, or gold alloy (Egerton, 2001). A connection should be established between the sample and the electrical connector and fine samples such as powders should be spread and completely dried on a conductor film such as aluminum (Al) paint. The samples should be free from liquids with high vapor pressure such as water, organic detergents, and residual oil films. Like previous phases, dry and powdered samples are used (Kaviani et al., 2010).

Electrolysis. Electrolysis is a method based on oxidation and reduction potentials of chemical elements. Molten salt electrolyte (calcium chloride, $CaCl_2$) and two electrodes made of graphite were used to separate Ti from other elements. Each electrode was attached to a pole by a conductive string placed in the electrolyte solution. It is noteworthy that, a power source ($I = 5$ A and $P = 3.1$ V) is used to provide the electric current. For this purpose, first the electrolyte is molten in 800°C, then, paint sludge powder sample is added (Jalaee, 2004).

Table 1. Humidity and weight of dry material of paint sludge

Mix	Verni sludge	Lining sludge	Quantity
60/19	45/56	41.3	Weight of sludge before drying (g)
17/66	17/6	16/84	Weight of dried material (g)
42/53	27/96	24/46	Humidity(g water)
70/65	61/36	59/22	Humidity (%)
29/35	38/64	40/78	Dried material (%)

Table 2. Results of XRF elemental test of paint sludge

Analyse	Concentration	Intensity
Na_2O	1.30 wt %	2.4
MgO	0.66 wt %	6.0
Al_2O_3	18.01 wt %	550.8
SiO_2	2.15 wt %	130.8
P_2O_5	0.28 wt %	45.0
SO_3	6.37 wt %	1687.0
Cl	600 ppm	10. 6
K_2O	550 ppm	11.2
CaO	2.30 wt %	536.2
TiO_2	54.21 wt %	17544.6
Cr_2O_3	2.44 wt %	1196.7
Fe_2O_3	0.43 wt %	304.4
Cu_2O	600 ppm	28.4
Zn	600 ppm	41.0
BaO	11.26 wt %	10528.1
Br	300 ppm	70.5
SrO	0.21 wt %	656.0
ZrO_2	350 ppm	117.2
Bi	750 ppm	72.4

XRF: X-ray fluorescence spectroscopy, Na_2O: sodium oxide, MgO: magnesium oxide, Al_2O_3: aluminum oxide, SiO_2: silicon dioxide, P_2O_5: phosphorus pentoxide, SO_3: sulfur trioxide, Cl: chlorine, K_2O: potassium oxide, CaO: calcium oxide, TiO_2: titanium dioxide, Cr_2O_3: chromium oxide, Fe_2O_3: iron oxide, Cu_2O: copper oxide, Zn: zinc, BaO: barium oxide, Br: bromine, SrO: strontium oxide, ZrO_2: zirconium oxide, Bi: bismuth.

Results

Amount and humidity (percentage) of paint sludge

Humidity and weight of final paint sludge includes a mixture of two types of sludge related to lining and verni processes (Table 1).

Table 3. Main combination of peak elements obtained from XRD test

Chemical formula	Existing combination	No
SiO_2	Silicium dioxide	1
TiO_2	Titanium dioxide	2
Al_2O_3	Aluminium dioxide	3
$BaSO_4$	Barium sulfate	4
FeS	Iron sulfide	5

XRF: X-ray fluorescence spectroscopy, Al_2O_3: aluminum oxide, SiO_2: silicon dioxide, TiO_2: titanium dioxide, $BaSO_4$: barium sulfate, FeS, iron sulfide.

Based on the calculations, 1 L of final sludge has a weight of 1377.25 g, with a dry weight of 404.22 g and a density of 1.37725 g/cm^3.

Results of XRF elemental test

Table 2 gives XRF results of primary analysis of dried paint sludge at 100°C.

Results of XRD combinational analytical test

With regard to XRF results, it can be concluded that three metals are the most abundant: Ti, Al, and Barium (Ba). In the next steps, XRD test is used for finding the type of elements (Table 3). Figure 1 shows the diagram that resulted from the test.

Results of temperature analysis (DTA) of paint sludge

With regard to results of temperature analysis test and the concerned diagram consisted of two curves of variations in matter in terms of temperature and variation in weight in terms of temperature, it is concluded that three permutations occur at 471°C, 596°C, and 767°C, respectively, while heating up to 1200°C with a heating rate of 20°C. To realize what changes and reactions occurred in paint sludge, and what combinations are remaining in each phase, XRD test was conducted. Thus, the paint sludge was heated to temperatures at which permutations were terminated (496°C, 613°C, and 850°C) and after each phase (precisely, after each permutation terminated and next one started), a sample was taken from the sludge, crushed in pounder, and XRF test was operated. Tables 4–7 show the results of these tests and Figure 2 shows the diagram resulting from the test.

It is noteworthy that the curve of weight variation in terms of temperature suggests that as the temperature reaches 1200°C the weight decreases to 80%.

Based on the percentage of combinations, XRF test (Tables 4–7) shows that as the temperature increases the levels of heavy elements decrease. Regarding the aim of this research, membrane and electrolysis

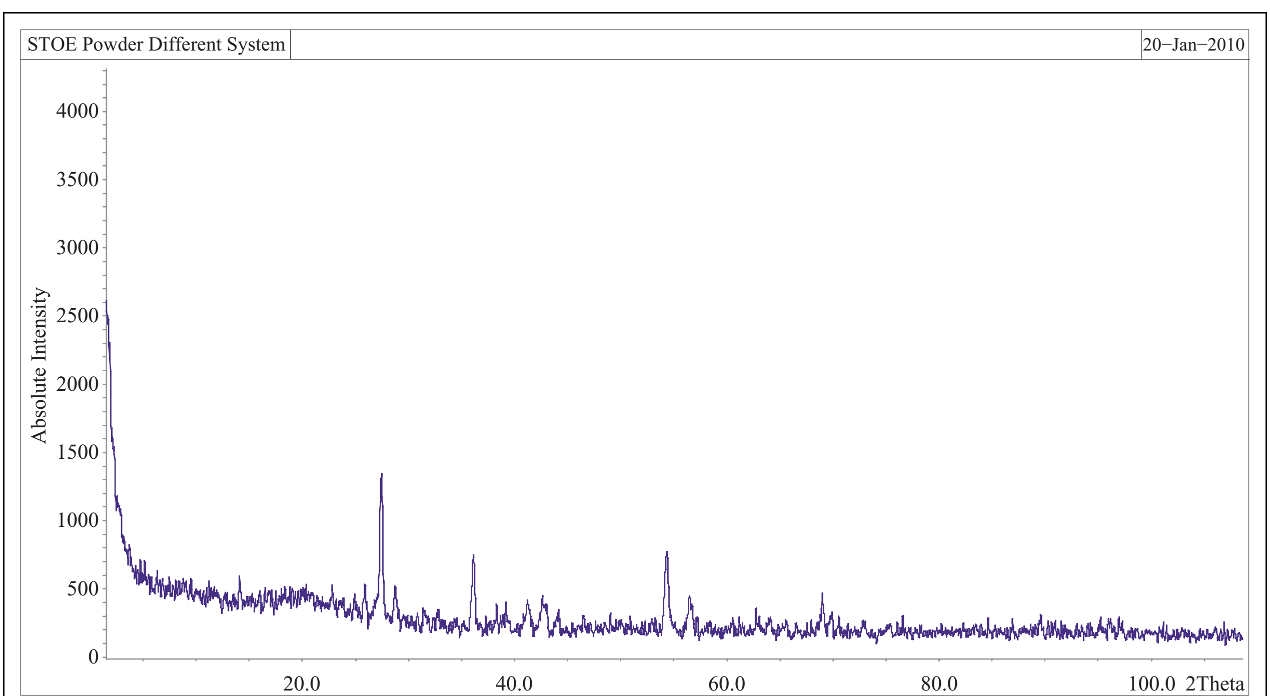

Figure 1. Diagram of X-ray fluorescence spectroscopy (XRD) test.

Table 4. Variations of matter in terms of temperature

Weight variation (%)	Weight (%)	Temperature	No
25	75/55	496	1
51/93	48/07	613	2
65/18	34/82	850	3
69/04	30/96	1200	4

Table 5. Percentage of paint sludge combinations, heated to 496°C

Analyse	Concentration
Na_2O	1.11 wt %
MgO	0.07 wt %
Al_2O_3	11.20 wt %
SiO_2	1.00 wt %
P_2O_5	0.331 wt %
SO_3	3.75 wt %
Cl	821 ppm
K_2O	0.02 wt %
CaO	1.40 wt %
TiO_2	26.27 wt %
Cr_2O_3	129 ppm
Fe_2O_3	0.15 wt %
L.O.I	47.27 wt %
Zn	54 ppm
BaO	7.03 wt %
Sr	1057 ppm
Cu_2O	99 ppm

Na_2O: sodium oxide, MgO: magnesium oxide, Al_2O_3: aluminum oxide, SiO_2: silicon dioxide, P_2O_5: phosphorus pentoxide, SO_3: sulfur trioxide, Cl: chlorine, K_2O: potassium oxide, CaO: calcium oxide, TiO_2: titanium dioxide, Cr_2O_3: chromium oxide, Fe_2O_3: iron oxide, Zn: zinc, BaO: barium oxide, Sr: strontium, Cu_2O: copper oxide.

were used to purify Ti from remaining elements, particularly Al and Ba. In order to conduct the membrane method, first SEM test was taken from paint sludge powder and was passed through UF filter in the form of a solution with distilled water. Figure 3 shows the diagram resulting from the SEM test and Table 8 shows the results of UF filter.

In order to conduct the electrolysis technique, paint sludge powder was mixed with sulfuric acid and the mixture was transmitted through the filter paper. It was observed that Ba remained on the filter in the form of a precipitate and Al and Ti passed through the filter. The solution beneath the filter paper was titered with sodium hydroxide (NaOH). Ti and Al were deposited on the filter. The deposit containing Al and Ti was dried and electrolysis was conducted. Table 9 shows the results of this test.

Table 6. Percentage of paint sludge combinations, heated to 613°C

Analyse	Concentration
Na_2O	1.71 wt %
MgO	0.88 wt %
Al_2O_3	33.44 wt %
SiO_2	1.79 wt %
P_2O_5	0.30 wt %
SO_3	7.55 wt %
Cl	600 ppm
K_2O	550 ppm
CaO	3. 03 wt %
TiO_2	35.18 wt %
Cr_2O_3	1.69 wt %
Fe_2O_3	0.34 wt %
BaO	13.74 wt %
Zn	600 ppm
Cu_2O	99 ppm
Sr	0.18 wt %

Na_2O: sodium oxide, MgO: magnesium oxide, Al_2O_3: aluminum oxide, SiO_2: silicon dioxide, P_2O_5: phosphorus pentoxide, SO_3: sulfur trioxide, Cl: chlorine, K_2O: potassium oxide, CaO: calcium oxide, TiO_2: titanium dioxide, Cr_2O_3: chromium oxide, Fe_2O_3: iron oxide, Zn: zinc, BaO: barium oxide, Sr: strontium, Cu_2O: copper oxide.

Table 7. Percentage of paint sludge combination, heated to 850°C.

Analyse	Concentration
Na_2O	1.37 wt %
MgO	0.63 wt %
Al_2O_3	32.67 wt %
SiO_2	1.71 wt %
P_2O_5	0.78 wt %
SO_3	7.45 wt %
Cl	350 ppm
K_2O	450 ppm
CaO	2.82 wt %
TiO_2	37.53 wt %
Cr_2O_3	0.89 wt %
Fe_2O_3	0.85 wt %
Zn	500 ppm
BaO	12.64 wt %
Sr	0.19 wt %

Na_2O: sodium oxide, MgO: magnesium oxide, Al_2O_3: aluminum oxide, SiO_2: silicon dioxide, P_2O_5: phosphorus pentoxide, SO_3: sulfur trioxide, Cl: chlorine, K_2O: potassium oxide, CaO: calcium oxide, TiO_2: titanium dioxide, Cr_2O_3: chromium oxide, Fe_2O_3: iron oxide, Zn: zinc, BaO: barium oxide, Sr: strontium.

Discussion and Conclusion

It is concluded that according to primary results of XRF test (Table 2), the paint sludge contains heavy

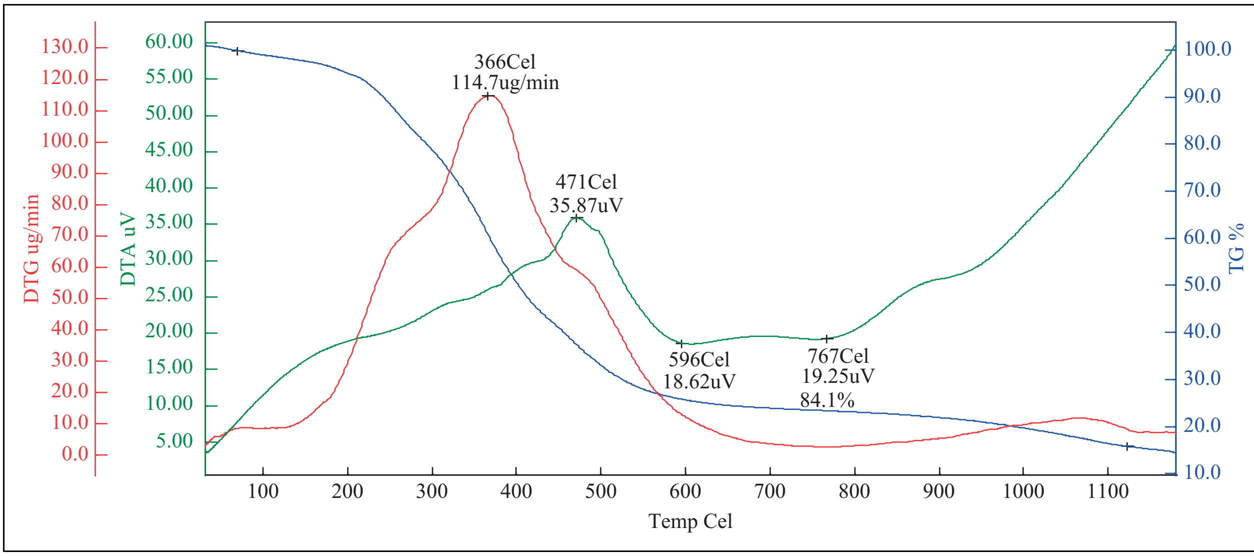

Figure 2. Temperature analysis of paint sludge in 20–1200°C (heating rate 20°C).

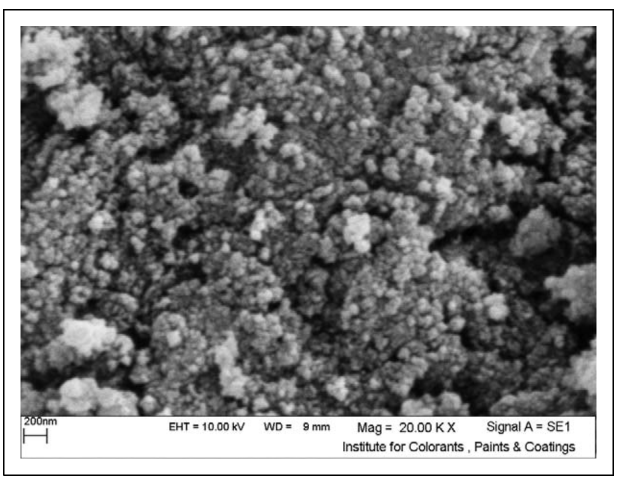

Figure 3. Scanning electron microscope (SEM) test from heated ash in 850°C.

elements that are toxic and hazardous, and the sludge has a high concentration of magnesium (Mg), Al, Ti, Ba, copper (Cu), iron (Fe), chromium (Cr), strontium (Sr), and so on.

Thus, finding scientific and applied solutions on which one can utilize updated techniques of eliminating paint sludge from car manufacturing industries and optimally use the remnants is a priority. The conclusion from the results of DTA test—which is carried out to identify permutations and reactions occurring in paint sludge at various temperatures—is that, heating at various temperatures can eliminate lethal organic combinations and heavy elements such as Cu, Cr, Mg, bromine (Br), and so on.

Table 8. The results of ICP test from the solution beneath UF membrane

Analyse	Concentration mg/L
Ti	65/11
Al	10/01
Ba	4/05

ICP: Inductively coupled plasma, UF: ultra filtration, Ti: titanium, Al: aluminum, Ba: barium.

Table 9. The results of test XRF following electrolysis

Analyse	Concentration
TiO_2	85.3 wt %
Al_2O_3	8.21 wt %
Na_2O	0.98 wt %
CaO	4.02 wt %
SiO_2	330 ppm
P_2O_5	0.87 wt %
SO_3	78 ppm

XRF: X-ray fluorescence spectroscopy, TiO_2: titanium dioxide, Al_2O_3: aluminum oxide, Na_2O: sodium oxide, CaO: calcium oxide, SiO_2: silicon dioxide, P_2O_5: phosphorus pentoxide, SO_3: sulfur trioxide.

During detailed and documented studies and continuous interaction with famous experts in metal extraction and advanced material synthesis, it was discovered that using two techniques of membrane and electrolysis for extracting Ti_2O, in addition to reduction of load of pollutants, economic benefits can be achieved. Ti_2O concentration is 65.11 mg/L in membrane technique and 85.3% by electrolysis. Therefore, it is noteworthy that lethal organic compounds and most heavy elements are eliminated by heating paint sludge according to the permutation temperature, and since Ti is a strategic element in paint production, electrolysis can be used to remove Ti from other elements remaining in the sludge with a high degree of purity (85.3%).

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Corrigendum

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http://omicron.ch.tuiasi.ro/EEMJ/

The authors would like to apologise for this error.