



## Treatment of a forging industry graphite-rich wastewater and sludge characterization

Viviana Nedel Reckziegel<sup>a,\*</sup>, Renan Fernando Tresoldi Thiesen<sup>a</sup>,  
Eduardo Osório<sup>b</sup>, Ivo André Homrich Schneider<sup>a</sup>

<sup>a</sup>Laboratory of Mineral and Environmental Technology, Department of Mining Engineering, Federal University of Rio Grande do Sul, Av. Bento Gonçalves, 9500, CEP: 91501-970, Porto Alegre, RS, Brazil, Tel. +55 51 33499388; email: viviana.reckziegel@gkndriveline.com (V.N. Reckziegel), Tel. +55 51 33087881; emails: renan.ftt@gmail.com (R.F.T. Thiesen), ivo.andre@ufrgs.br (I.A.H. Schneider)

<sup>b</sup>Laboratory of Siderurgy, Department of Metallurgical Engineering, Federal University of Rio Grande do Sul, Av. Bento Gonçalves, 9500, CEP: 91501-970, Porto Alegre, RS, Brazil, email: 00098920@ufrgs.br

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### ABSTRACT

The objective of this work was to study wastewater treatment and characterize sludge generated at a forging industry using a water-based graphite lubricant. Initially, wastewater was treated by coagulation/flocculation with poly-aluminum chloride and a cationic flocculant. The treatment substantially reduced the pollutant load, exceeding the efficiency for most parameters assessed by 90%. The sludge generated in the wastewater treatment plant was characterized in terms of microstructure, particle size distribution, chemical and mineralogical composition, and by immediate analysis as a solid energetic material. The sludge is composed of mainly graphite particles and, after dehydration, resulted in a material with possibilities for safe discharge, recycling or reuse.

*Keywords:* Sludge; Water treatment; Graphite; Forging

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### 1. Introduction

Base industries, such as steel production, have high pollution potential [1]. Among the activities carried out by industries in this sector, we highlight forging, where steel is processed under high temperatures, which results in its conformation to the desired shape. During forging, it is necessary to apply a lubricant in order to reduce metal-metal friction, and enables the removal of the forged part from the matrix, as well as cooling, protecting and extending the useful life of the matrices [2–6].

The process of forging presents economic advantages, as no part of the worked metal is wasted [7–9]. However, it involves the generation of gas emissions, effluents and different wastes that present potential risks to the employees'

health and to the environment [10]. As the conformability of the material and the defects that are formed are directly affected by lubrication during production, the feasibility and productivity of a forging process strongly depend on the supplied lubricant [11].

Solid lubricants are generally used as additives to liquid or pasty lubricants. They are sometimes applied in suspension, so that the liquid phase evaporates during the application. Lubricants for conventional metal conformation are generally classified into four categories: oil-based graphite, water-based graphite, synthetic and solid-based. In forging operations, graphite-based lubricants have lower costs and greater resistance to high pressures and temperatures, and are the most common, being employed in approximately 80% of forges. These lubricants are traditionally composed of an

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\* Corresponding author.

oil-based graphite emulsion and, more recently, of water-based graphite suspension [12].

After a few cycles in the conformation process, these lubricants are disposed of, along with the wash water from machines, matrices, floors and other waste waters, generating a complex effluent, which must be treated in order to meet emission parameters established by law.

In a steel mill that produces auto parts, located in the state of Rio Grande do Sul, in the Federal Republic of Brazil, there is a forging operation that has employed oil-based graphite lubricants for the last two decades. The treatment of the resulting effluent was always complex, requiring high doses of reagents. The wastewater treatment process has been based on emulsion breakage by adding large amounts of sulfuric acid and hydrogen peroxide, followed by neutralization with sodium hydroxide, flocculation and decantation. In addition to high consumption and hazard levels posed by the employed reagents, the efficiency of the treatment is low. Furthermore, one of the greatest issues is in relation to sludge management. The sludge, which is a mix of graphite, oil, water and other impurities, is a pasty, sticky material that is difficult to handle. It is not suitable for filtering, so it has to be transferred in its wet form to a highly specialized waste receiver and processor in Brazil, located a thousand kilometers from the company.

Oil-based graphite lubricant has recently been substituted by a similar water-based graphite lubricant. This substitution significantly changed the composition of the effluent, which became a suspension of very fine graphite particles in water, different from the commonly treated oil-based emulsion. The treatment of this effluent has proven to be easier; however, little is known about the characteristics of the sludge and its end-use possibilities.

Thus, the purpose of this article is to study the treatment of a forging industry wastewater operating with a water-based graphite lubricant. The sludge characteristics, its handling and final destination or reuse possibilities were assessed. In terms of composition, the sludge is rich in graphite. Recent studies have shown great potential for the use of materials containing graphite [13–17] and this shall be addressed in this article. It is worth highlighting that literature on the treatment of effluents from forging operations is still scarce. Likewise, few studies about graphite wastes are described. Therefore, this research meets one of main challenges of mechanical and steel-based industries, which is improving productive processes for an efficient environmental protection policy.

## 2. Materials and methods

### 2.1. Effluent

The study was carried out using a sample of forging effluent derived from the production of side shafts, fixed joints and plunging joints for vehicles. In this operation, the lubricants go through a 1:1 water dilution and go to the press storage tanks. The lubricant emulsion is sprayed on the parts seconds before their conformation. Then the lubricant is disposed of and goes to accumulation tanks, where it is mixed with wash waters derived from the forging plant. After reaching a certain volume, it is forwarded to the effluent treatment station.

According to the supplier, the physical–chemical characteristics of the water-based lubricant are: color – dark gray; appearance – homogeneous fluid; graphite content –  $\geq 10\%$ ; pH of the suspension –  $\geq 10$ ; density of the suspension –  $1.1 \text{ g cm}^{-3}$ ; viscosity at  $40^\circ\text{C}$  –  $1,500 \text{ mPa s}^{-1}$ ; average particle size –  $4 \mu\text{m}$ .

### 2.2. Reagents

The pH adjustments were made by the addition of NaOH. The coagulant used, poly-aluminum chloride (PAC), was dosed from a stock solution of  $90 \text{ g Al L}^{-1}$ . These reagents were all of commercial grade. The polymeric flocculant used was Nalco 9909, a powdered cationic polyacrylamide of high molecular weight. The polymer was prepared in a stock solution concentration of  $1 \text{ g L}^{-1}$  and used between 24 and 48 h after preparation.

### 2.3. Physico-chemical characterization

Particle size distribution analysis of the suspended solids was carried out using a laser diffraction method with a Cilas Particle Size Analyzer 1180. The electrokinetic properties of the graphite particles in the effluent were investigated using a Zeta Potential Analyzer, model ZetaPlus (Brookhaven Instruments Corporation, United States) and pH was adjusted by the addition of  $\text{HNO}_3$  and KOH. Surface tension was determined by the du Noüy ring detachment method using a Kruss tensiometer (model 8451), according to the standard ASTM D1590 [18].

### 2.4. Waste water analysis

The analyses carried out in this work were the water quality parameters established in the Operating License (OL) of the local Regulating Environmental Agency: pH, settleable solids, suspended solids, chemical oxygen demand (COD), biochemical oxygen demand ( $\text{BOD}_5$ ), total Kjeldahl nitrogen, total phosphorus, sulfides, aluminum, boron, lead, copper, iron, nickel, zinc, oils and greases. All methods used were performed according to Standard Methods for the Examination of Water and Wastewater [19].

### 2.5. Batch bench-scale studies for wastewater treatment and sludge preparation

Initial studies of sludge characterization were carried out at laboratory scale. A composite sample of 5 L of wastewater, representing the three shifts of production, was collected. One liter of this effluent was treated in a jar test apparatus with the dosage commonly applied in an industrial plant ( $360 \text{ mg Al L}^{-1}$  in the form of PAC, pH adjustment to 6.5 and the addition of  $25 \text{ mg L}^{-1}$  of a high molecular weight cationic polyacrylamide). The sludge generated in the batch bench-scale experiment was submitted to 1 h sedimentation in an Imhoff Cone according to ASTM D3977 [20]. After that, the supernatant was removed with the aid of a siphon for water analysis in accordance with the parameters established in the Operating License (OL) of the Regulating Environmental Agency. The sludge remaining in the Imhoff Cone was vacuum filtered, oven-dried at  $60^\circ\text{C}$ , pounded to break up the

clods, and then weighed. Part of the sludge was submitted to a pressure of 100 MPa, in a mechanical press, resulting in a cylinder of compacted solids with a diameter of 1 cm.

## 2.6. Sludge characterization

The sludge generated in the treatment was analyzed qualitatively and quantitatively regarding the settled volume in the Imhoff Cone – ASTM D3977 [20]; specific mass – ASTM D854 [21]; moisture content – ASTM D2216-10 [22]; ash, volatile matter and fixed carbon content – ASTM D3172-07 [23]; calorific value (CV) – ASTM D2015-00 [24]; elemental analysis – USEPA 3051a [25], USEPA 3050B [26] and ASTM D5373-02 [27]; and leaching characterization according to Brazilian Standard NBR 10004 [28].

X-ray diffraction was carried out in a Siemens (Bruker AXS, United States) X-ray diffractometer, model D-5000 ( $\theta$ - $\theta$ ), equipped with a curved graphite monochromator in the secondary beam and a fixed Cu anode tube, operating at 40 kV and 40 mA, with an incident radiation of 1.5406 Å. The angular range analyzed was from 5° to 100° 2 $\theta$  with a step size of 0.05°s<sup>-1</sup> using divergence and anti-scattering slits of 1° and 0.2 mm in the detector. Scanning electron microscopy and elemental analysis by energy-dispersive spectroscopy (EDS) was performed using a microscope – model MEV EVO MA10, Carl Zeiss (Germany). Thermogravimetric analysis was conducted in a Netzsch STA 409PC thermobalance under an oxidizing atmosphere composed of synthetic air, flowing at a rate of 100 mL/min. An alum plate crucible with a heating rate of 30°C/min to the maximum temperature of 1,000°C was used.

## 2.7. Effluent treatment at full-scale

Finally, results attained in full-scale were gathered. The configuration of the treatment of the water-based lubricant effluent is presented in Fig. 1. The plant works in batch steps of 20 m<sup>3</sup>, allowing for treatment of the approximately 105 m<sup>3</sup> of forging wastewater that are generated per month. Coagulation/flocculation and gravity settling processes are carried out in the same tank. The effluent is homogenized by the injection of compressed air, which then receives the PAC, the pH is adjusted, and a flocculant is added. The

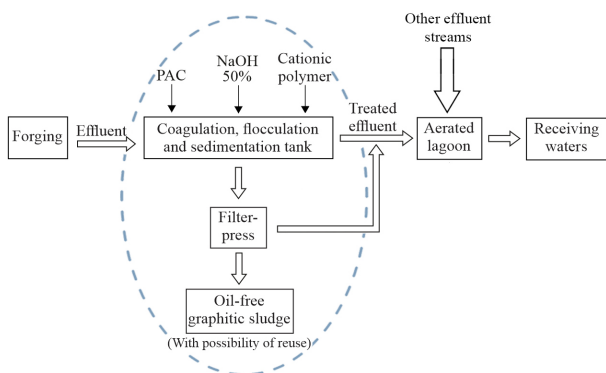


Fig. 1. Schematic representation of the steps of the treatment station operating with the effluent derived from water-based lubricant.

flocs are allowed to settle for a period of 12 to 15 h and the sludge is removed from the bottom of the basin. This graphite-rich sludge is dewatered in a filter press and is the subject of the present study. The treated effluent, after this physico-chemical process, is sent to an aerated pond which receives this and other effluent streams (such as sewage from toilets and water from wash-basins and floor outlets) from the forging complex before discharge into receiving waters.

Quantification of the sludge used the average data of effluent generated by the company and the assessment of the destination and recycling possibilities were evaluated under regional and national contexts.

## 3. Results and discussion

### 3.1. Effluent characterization

The effluent stream entering the wastewater treatment plant is of variable composition (Table 1). Variations in chemical, physical and physico-chemical properties of the stream arise from week-to-week variations in the operation of the forging process. The effluent is an aqueous suspension of high solids content. Solids are present in colloidal or very fine particle sizes, in the range of 1.9 to 13.6  $\mu\text{m}$  (with a  $D_{50}$  of 5.9  $\mu\text{m}$ ) and, thus, should be aggregated by coagulation/flocculation to be removed by a gravity settling separation process.

Fig. 2 shows the electrokinetic behavior of three different samples of the graphite particles suspended in the effluent as function of pH. The curves indicate a negative charge for the particles in a pH range from 2 to 10. These results are in close agreement with past studies with graphite particles carried out by Wakamatsu and Numata [29]. This negative charge explains the stability of the suspension, basically promoted by electrostatic repulsion. Graphite is also considered to be a hydrophobic

Table 1  
Physico-chemical properties of the raw effluent

Parameter	Water-based lubricant
Color	Dark gray to black
Appearance	Homogeneous fluid
Surface tension (25°C)	40–59 mN m <sup>-1</sup>
Temperature	20°C–25°C
Suspended solids	6,000–24,000 mg L <sup>-1</sup>
Average particle size range	1.9–13.6 $\mu\text{m}$

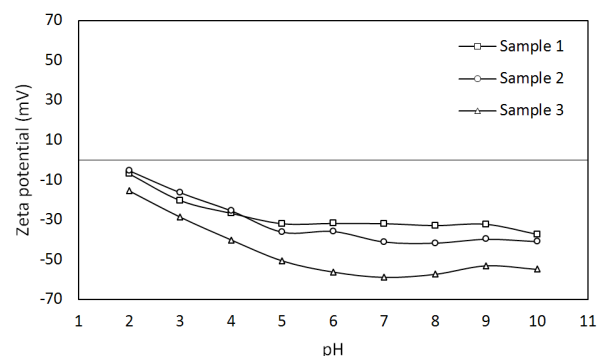


Fig. 2. Zeta potential of the suspended solids as a function of pH.

material. However, the particles present good wettability and dispersion in the suspension, probably as a result of dispersing agents present in the lubricant composition. Therefore, the addition of coagulation and flocculation reagents is required for the successful aggregation of the particles.

### 3.2. Batch bench-scale study

The analysis of the raw and treated wastewater sample derived from the forging operation used to characterize the sludge at the laboratory is shown in Table 2. This sample is very representative of plant scale, as will be further seen in the full-scale results. It showed a high concentration of suspended solids, COD, BOD<sub>5</sub>, total nitrogen, and oils and greases. The value of 0.37 of the COD/BOD<sub>5</sub> ratio is considered low, indicating that a significant portion of organic matter is not biodegradable (in this case, graphite). The metals that appear in larger concentrations are iron and aluminum, followed by the metalloid boron. Treatment showed high efficiency for suspended solids removal, which is reflected in many water quality parameters. However, the effluent still has concentrations of COD, BOD<sub>5</sub>, soluble nitrogen and boron, which demand a subsequent treatment step. This step is carried out at the company site, in an aerated lagoon; however this is not the subject of the present article.

After destabilization with 360 mg Al L<sup>-1</sup> in the form of PAC and 25 mg L<sup>-1</sup> of cationic polymer, the volume settled in the Imhoff Cone was measured. Sedimentation for 1 h generated 450 mL of sludge per liter of treated effluent (55% of the volume of the effluent in clarified form) and when the period was extended to 24 h, the volume was 400 mL (60% of the volume of effluent in clarified form). The treatment with PAC generated a sludge mass of 17.1 g L<sup>-1</sup> of treated effluent (1.7% [m/V]). As we can see, the sludge contains high amounts of water, which makes its disposal difficult and expensive. However, after the vacuum filtering process, the average

content of solids reached 10.8% (m/V). Fig. 3 illustrates the procedure, showing the sludge generated in the treatment process with PAC and cationic flocculant in the Imhoff Cone (a), after filtering (b), and after a step of drying in an oven at 60°C and clod breaking (c), and after compaction (d).

### 3.3. Sludge characterization

After crushing, the dry sludge assumes the form of powder. The apparent specific mass of the material is 0.356 g/cm<sup>3</sup>. After the process of pressing at 100 MPa (Fig. 3(d)), the material was consolidated and changed to a specific mass of 1.8 g/cm<sup>3</sup>, closer to the specific mass of pure graphite, which is 2.1–2.2 g/cm<sup>3</sup> [30,31]. This nearly 500% increase in the specific mass of the material suggests that compaction of the sludge can be an alternative that decreases costs related to the storage, transportation and disposal of this material, as the costs are related to the volume of material.

The dry sludge was observed in the scanning electron microscope, showing a prevalence of flat particles in the granulometric range of a few micrometers (Fig. 4). With the EDS analysis (Fig. 5), it was possible to identify the prevalence of carbon with minor amounts of iron, aluminum, oxygen and silicon. Fig. 5 depicts the EDS spectrum of one of the many analyses carried out with very similar behavior.

The results of the analysis regarding leaching and classification according to NBR 10004 show that the sludge of the forging effluent is classified as CLASS II-A NON-INERT RESIDUE. According to the standard, the sample neither shows characteristics of corrosivity, reactivity, flammability, pathogenicity nor toxicity.

The results of the elemental analysis of the sludge are presented in Table 3. There is a carbon content of 70.7%, 4.8% iron, 1.6% aluminum and approximately 21% oxygen. The presence of iron could be associated to ferrous losses or ferrous-graphite impregnation in the forging process and

Table 2

Parameters of raw and treated effluent with PAC at bench scale as well as removal efficiency of the defined treatment

Parameter	Effluent		OL standard	Efficiency (%)
	Raw	Treated		
BOD <sub>5</sub> (mg L <sup>-1</sup> )	6,120	610	≤110	90.0
COD (mg L <sup>-1</sup> )	16,583	1,650	≤330	90.1
Total phosphorus (mg L <sup>-1</sup> )	2	<LoQ <sup>a</sup>	≤3.0	100
Total Kjeldahl nitrogen (mg L <sup>-1</sup> )	295	160	≤10	45.8
Suspended solids (mg L <sup>-1</sup> )	7,870	12	≤125	99.8
Sulfides (mg L <sup>-1</sup> )	<LoQ	<LoQ	–	100
Aluminum (mg L <sup>-1</sup> )	163.1	0.188	–	99.9
Boron (mg L <sup>-1</sup> )	50.6	39.2	≤5.0	22.5
Lead (mg L <sup>-1</sup> )	<LQ	0.102	–	–
Copper (mg L <sup>-1</sup> )	1.25	0.093	≤0.5	92.6
Iron (mg L <sup>-1</sup> )	37.1	<LoQ	≤10	100
Nickel (mg L <sup>-1</sup> )	<LoQ	0.017	≤1.0	–
Zinc (mg L <sup>-1</sup> )	1.35	<LoQ	≤2.0	100
Oils and greases (mg L <sup>-1</sup> )	300	<LoQ	≤10	100
pH	9.63	6.40	6.0–9.0	–

<sup>a</sup> Measured value was below the limit of quantification of the applied technique.



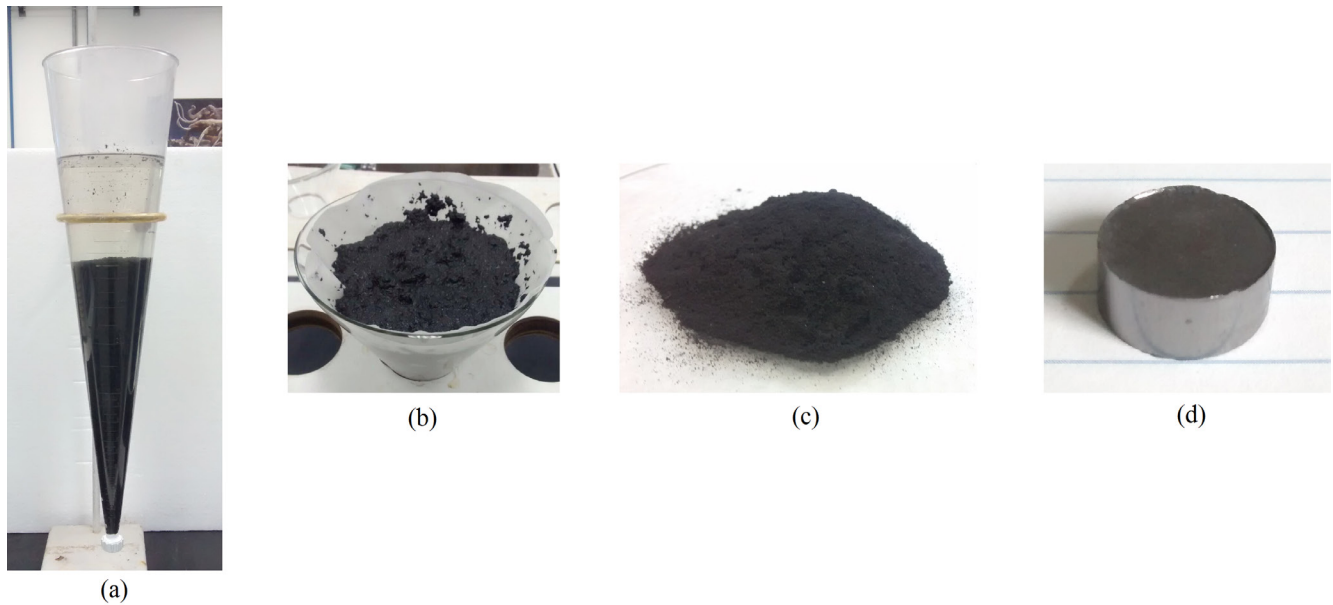


Fig. 3. Settled sludge after bench treatment in the Imhoff Cone (a); after filtration (b); after drying at 60°C and clod breaking (c); and after compaction at 100 MPa (d).

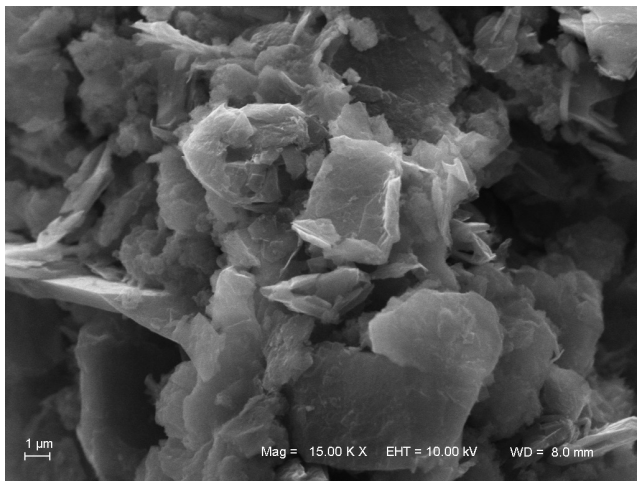


Fig. 4. Scanning electron microscopy image of graphite sludge derived from the bench treatment of a forging effluent that applies a water-based graphite lubricant.

the presence of aluminum by PAC addition in the coagulation process. Other minor elements were found in very small amounts (less than 1%): sulfur, nitrogen, chlorides, fluorides, phosphorus, arsenic, boron, cadmium, calcium, lead, cobalt, copper, chromium, magnesium, manganese, mercury, nickel, potassium, silicon, sodium and zinc. The sulfur content was 0.33% and nitrogen was 0.21%.

The diffractogram obtained by the X-ray diffraction (XRD) technique for sludge with PAC is shown in Fig. 6. It is possible to see that the prevalent crystalline species is graphite, followed by quartz. These results are in agreement with the EDS readings for the material, which showed a predominance of carbon, silicon and oxygen. The presence of a high intensity diffraction peak at  $2\theta$  at 26.56°, corresponding to the basal spacing of 0.335 nm, is characteristic of pure

graphite. However, a mild oxidation of graphite, which is demonstrated by the peak at  $2\theta$  of 10° [32] was noted.

Sludge generated from the laboratory treatment of the forging effluent treated with PAC has a carbon content above 70%. The material is rich in graphite, which opens a range of possibilities for its destination, such as: lubricants, electrodes, power material for cement kilns and thermoelectric plants and diamond synthesis. However, considering the regional context and production scale, it was initially decided to assess the energetic potential of the material. In the same city as the company, there is a coal thermal electric power plant that could be a potential receiver of the waste.

Therefore, the dry sludge was also submitted to immediate and CV analyses (Table 4). The ash content in the generated sludge was 21.4% and the volatile matter content was 9.0%. These data indicate a carbonification level similar to a semi-anthracite [33]. The high level of carbonification of the material associated with moderate ash content resulted in a material with high CV, on the order of 24,493 J g<sup>-1</sup>. For comparison purposes, this material exceeds the specifications of the local thermoelectric plant, which burns coal with an ash content of 53%, a sulfur content between 0.8% and 1.3%, CV of 13,000 J g<sup>-1</sup> and 15% moisture content [34]. Other materials employed for power purposes in the region are eucalyptus sawdust (17,354 J g<sup>-1</sup>) and rice husk ash (16,663 J g<sup>-1</sup>) [35–37].

These results are confirmed by thermogravimetric analysis, which enables analyzing the variation of the mass as a function of time and temperature (Fig. 7). The test was carried out in an oxidizing atmosphere until a temperature of 1,000°C was reached. It is possible to see, in this figure, that a significant loss of mass occurs only above 600°C. From 600°C to 1,000°C, the sample lost more than 80% of its total mass (about 100% of its combustible fraction), a typical behavior of thermal decomposition of most graphite materials [38]. The remaining mass of the sample derived from the PAC treatment, approximately 20%, is similar to the ash analysis.

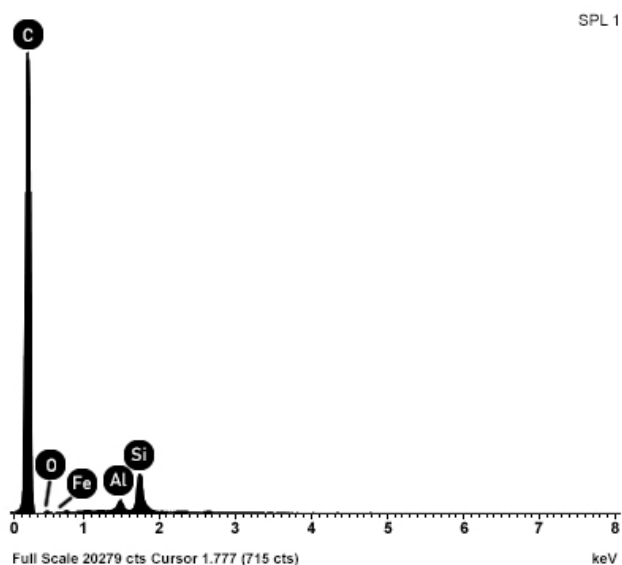


Fig. 5. EDS spectrum of sludge derived from the bench treatment of a forging effluent that applies a water-based graphite lubricant.

### 3.4. Industrial performance of the wastewater plant

Table 5 lists the means, minimum and maximum values, and the standard deviations of several water quality parameters of the raw and treated wastewater at full-scale with respect to 12 batch treatment operations. There is a great variability in the wastewater inflow, which can be explained by variations in the amount of wash water used to clean the machines in the forging process as well as eventual hydraulic oils leaks. Nevertheless, the treatment efficiency is similar to those attained at laboratory scale for most parameters and the effluent treatment station performs the purpose of suspended solids, metal and oil and grease removal. There is also a substantial decrease in the organic load (in terms of BOD<sub>5</sub> and COD) and nutrients (N and P), reducing the pollutant load for the biological process that follows. Of all wastewater parameters, boron is the most difficult to lower, since its removal indices by coagulation/flocculation are low [39].

Using a monthly effluent flow of 105 m<sup>3</sup> month<sup>-1</sup>, the mass of sludge to be managed is approximately 30 t month<sup>-1</sup> of filtered sludge with about 50% moisture content. This material can be dried, generating about 15 t month<sup>-1</sup> of dried graphitic sludge. The mean and standard deviation of the CV, ash, volatile matter and fixed carbon of seven samples are listed in Table 6. These results are also in agreement with the results attained with the sludge previously generated and characterized at laboratory scale and validates its potential for co-firing in energy production.

Finally, it should be mentioned that there has been an evolution of sludge management derived from forging wastewaters. In this specific case, the sludge generated in the past, with the wastewater derived from oil-based lubricants, was transported without filtration to long distances for processing, leading to high costs. The change in lubricants from oil-based to water-based simplified the wastewater treatment process and generated a sludge that can be filtered, dried and compacted, reducing storage, transportation and disposal costs. The characteristics of this liquid phase-free sludge

Table 3

Elemental analysis of the sludge generated in the bench treatment of a forging effluent that contained a water-based graphite lubricant

Element	Amount (%)
Carbon	70.73
Hydrogen	0.64
Nitrogen	0.21
Sulfur	0.33
Chlorides	0.36
Fluorides	–
Total phosphorus	–
Aluminum	1.59
Arsenic	–
Boron	0.02
Cadmium	–
Calcium	0.03
Lead	0.002
Cobalt	0.0005
Copper	0.0177
Chromium	0.0131
Iron	4.75
Magnesium	0.008
Manganese	0.038
Mercury	–
Nickel	0.004
Potassium	0.020
Silicon	–
Sodium	0.181
Zinc	0.006
Oxygen	21.04
Total	100%

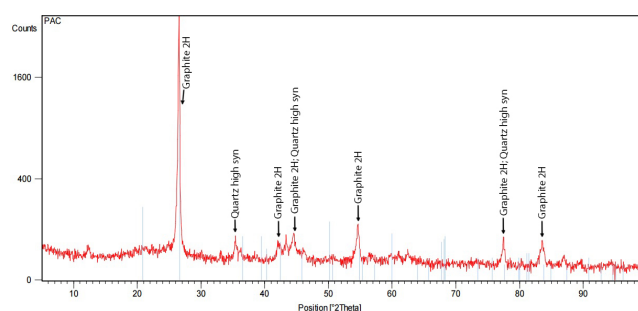


Fig. 6. Diffractogram referring to the XRD analysis of the sludge generated in the bench treatment of a forging effluent that contained a water-based graphite lubricant.

permitted sending the material to nearby cement kilns, partially reducing the costs associated with its destination. However, after sludge characterization, other uses could be considered, including the co-firing of the material. Perhaps, in the near future, there will be no costs associated with the destination of this sludge, but rather profits. The automotive sector, as a whole, seeks to find markets that could increase

Table 4  
Calorific value and immediate analysis and of the sludge generated in the bench treatment of the forging effluent (using water-based lubricant) with PAC (dry basis)

Parameter	Water-based sludge
Calorific value ( $\text{J g}^{-1}$ )	24,493
Ash (%)	21.4
Volatile matter (%)	9.0
Fixed carbon (%)	69.6

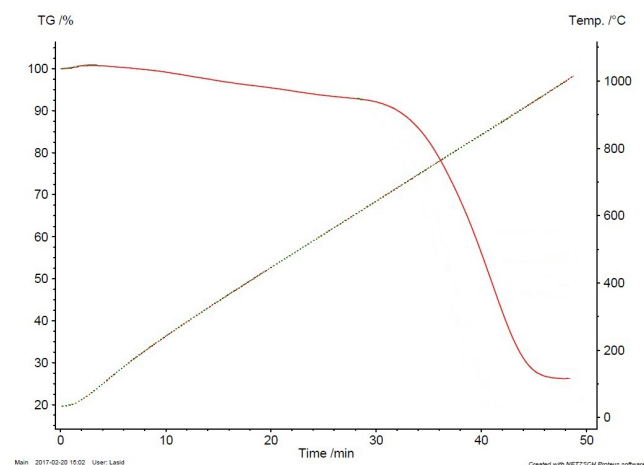


Fig. 7. Thermogravimetric analysis of sludge generated in the treatment of forging effluent (using water-based lubricant) with PAC.

Table 5  
Mean, standard deviation, maximum and minimum values of the water quality parameters for the raw and treated effluent at industrial scale, as well as the removal efficiency. Number of samples  $n = 12$ .

Parameter	Raw effluent ( $\text{mg L}^{-1}$ )				Treated effluent ( $\text{mg L}^{-1}$ )				Mean efficiency (%)
	Mean	Maximum	Minimum	Standard deviation	Mean	Maximum	Minimum	Standard deviation	
BOD <sub>5</sub>	32,893	115,290	2,090	31,459	2,088	4,420	424	1,193	93.7
COD	89,684	312,766	5,660	85,229	5,696	11,966	1,150	3,224	93.6
Total phosphorus	6.24	27.85	<0.01	7.75	2.46	9.20	<0.01	3.07	60.5
Total Kjeldahl nitrogen	844.85	2,128	295	603.23	300.58	551.0	160	122.15	64.4
Suspended solids	18,242	79,167	550	22,766	355	1,600	11	480	98.1
Sulfides	1.10	6.90	<0.002	1.94	0.06	0.32	<0.002	0.09	94.5
Aluminum	56.80	163.10	9.15	40.87	12.83	60.55	0.17	17.22	77.4
Boron	77.87	248.45	7.35	71.59	43.35	83.0	8.20	20.65	44.3
Lead	0.267	1.20	<0.006	0.427	0.006	<0.006	<0.006	0	97.7
Copper	5.158	13.10	0.150	3.689	0.610	2.750	0.040	0.849	88.2
Iron	515.96	2814.50	37.10	777.10	23.90	124.90	<0.060	34.60	95.4
Nickel	0.580	2.0	<0.010	0.802	0.372	1.050	<0.010	0.374	35.8
Zinc	9.588	55.60	0.80	14.292	1.978	10.90	<0.050	3.595	79.4
Oils and greases	3,724	12,090	160	3,455	70	284	<10	89	98.1

opportunities for a proper destination for all waste materials of the productive chain.

#### 4. Conclusions

The substitution of an oil-based graphite lubricant for a water-based graphite lubricant in the forging plant allowed the treatment of the associated effluents by simple colloidal/fine particle destabilization and a gravity settling process. The procedure was successfully attained with the aid of PAC and a high molecular weight cationic polyacrylamide. The treatment substantially reduced the pollutant load, with a removal efficiency of over 90% for most parameters assessed. The change of lubricant enabled the generation of a sludge that can be easily filtered and handled. It has 70% carbon content, mainly in the form of graphite, with a certain level of oxidation. An ash content of about 20% and a CV in the order of  $24,493 \text{ J g}^{-1}$  allow this material, in a regional context, to be

Table 6  
Mean and standard deviation of calorific value, ash, volatile matter and fixed carbon (dry basis) of the sludge generated in the treatment of the effluent at industrial scale. Number of samples  $n = 7$

Parameter	Mean	Standard deviation
Calorific value ( $\text{J g}^{-1}$ )	24,882	1,260
Ash (%)	18.7	6.5
Volatile matter (%)	19.6	11.3
Fixed carbon (%)	61.7	16.1

employed for cement kilns or power generation. However, other application alternatives are being investigated, including its cleaning and return to the lubrication process.

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