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

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Forging is a manufacturing process involving the shaping of metal using localized compressive forces. It is necessary to apply a lubricant, in many cases composed by graphite, and the process generate a wastewater that requires a proper treatment. The objective of this study was to evaluate the efficiency of the treatment of such effluent and characterize the sludge generated at a forging industry that recently changed in industrial process the oil-based lubricant by water-based lubricants. Initially, wastewater was treated by coagulation/flocculation with poly-aluminum chloride and a cationic flocculant. The treatment substantially reduced the pollutants load, exceeding in 90% the efficiency for most parameters assessed. The sludge generated in the wastewater treatment plant was characterized in terms of its microstructure, particle size distribution, chemical and mineralogical composition, and immediate analysis in terms of a solid energetic material. The sludge is composed mainly by graphite particles and, after dehydration, resulted in a material with possibilities for safe discharge, recycling or reuse. Considering the amount of sludge generated and the regional context, one possibility for destination is as energetic material for electric power generation.

Keywords: sludge, water treatment, graphite, forging.

Introduction

Base industries, such as steel, have a high polluting potential [1]. Amongst the activities carried out by industries in this segment, we highlight forging, where steel is processed in presses, under high temperatures, which results in its conformation in the desired shape. During the forging, it is necessary to apply a lubricant, in order to reduce the metal-metal friction, aiming at enabling the removal of the forged part from inside the matrix, as well as to cool, protect and extend 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 generation of gas emissions, effluents and different waste that present potential risks for the employees' health and for the environment [10]. As the conformability of the material and the defects that are formed are directly affected by lubrication during the production, the feasibility and productivity of a forging process strongly depend on the supplied lubrication [11].

Solid lubricants are used, in general, as additives to liquid or pasty lubricants. They are sometimes applied in suspension, so that the liquid means 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, for having lower cost and great resistance to high pressures and temperatures, are the most common, being employed in approximately 80% of the forges. These lubricants are historically composed by an oil-based graphite emulsion and, more recently, by water-based graphite particle suspensions [12].

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

In a steel mill that produces auto parts, located in the state of Rio Grande do Sul, in the Federative Republic of Brazil, there is a forging industry that, for the last two decades, has employed oil-based graphite lubricants. The treatment of the resulting effluent was always complex, requiring high doses of reagents. The process is 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 regarding sludge management. 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 carried in its wet form to the state of Paraná, locate a thousand kilometers of the company.

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

Thus, the purpose of this article is studying the sludge generated from the treatment of the effluent using water-based lubricant. The sludge characteristics, its handling and final destination or reuse possibilities were assessed. Regarding its composition, it is known that sludge is rich in graphite. Recent studies have shown great potential of usage of materials or waste containing graphite [13-17] and that shall be approached in this article. It is worth highlighting that literature on the treatment of effluents of forging operations is still scarce. Likewise, few studies about graphite waste are described. Therefore, this research meets one of main challenges of mechanic and steel base industries, which is adding improvements in productive processes to an efficient environmental protection policy.

2 Materials and Methods

The study was carried out in a sample of forging effluent deriving 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 goes to the storage tanks of the presses. 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 washing waters derived from forging plant. After reaching a certain volume, it is forwarded to the effluent treatment station. The Table 1 shows some of the physical-chemical characteristics of the water-based lubricant.

Table 1 - Physical-chemical characteristics of the water-based graphite lubricants used in the forging process. Source: lubricant manufacturing companies: Henkel.

Parameter	**Water-based lubricant**
Color	Dark gray
Appearance	Homogeneous fluid
Graphite content	>=10%
pH of the emulsion	>=10
Density at 20 °C	1.1 g/cm³
Viscosity cSt at 40 °C.	1500 mPa.s
Average particle size	4 µm

The water-based effluent is treated by a physical-chemical procedure in a single step. The effluent is neutralized, homogenized with the injection of compressed air, and then it receives the polyaluminum chloride (PAC) as coagulant and a cationic polymer for flocculation. The dosage of reagents typically applied is 360 mg Al/L in the form of PAC, pH adjustment to 6.5 and 25 mg/L of flocculant (cationic polyacrylamide). The sludge rich in graphite is dehydrated in a filter-press and stored. The treatment lasts an average of 8 to 16 hours. The configuration of the treatment of the water-based effluent is presented in the Figure 1.

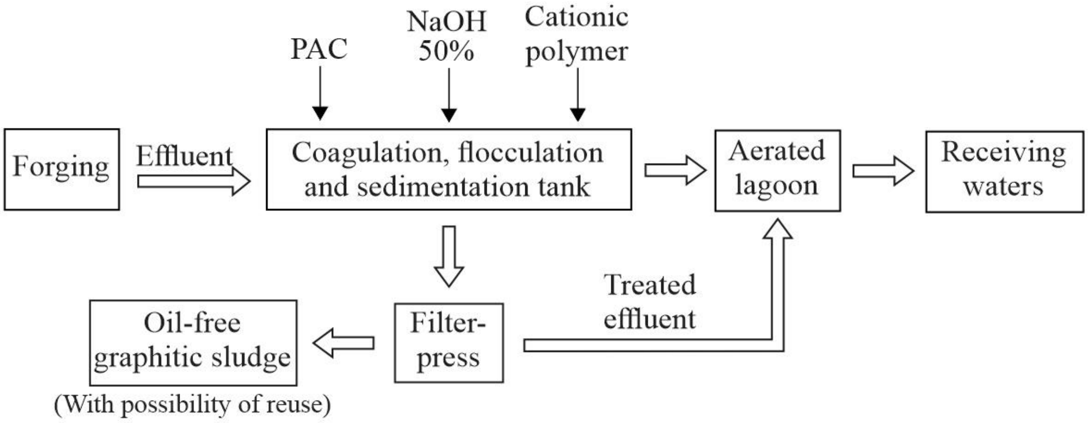


Figure 1. Schematic representation of the steps of the treatment station operating with the effluent derived from water-based lubricant.

The sample was collected during the three shifts of production, in a total of 5 liters of effluent. The effluent was treated with the same dosage applied in an industrial plant (360 mg Al/L in the form of PAC, pH adjustment to 6.5 and adding 25 mg/L of a high molecular weight cationic polyacrylamide). The average concentration of pollutants in the raw and treated effluent were analyzed regarding the following parameters of water quality: pH, DBO_5, DQO, total phosphorus, total Kjeldahl nitrogen, suspended solids, sulfides, aluminum, boron, lead, copper, iron, nickel, zinc, oils and greases. The analysis followed the methodology described in Standard Methods for Water and Wastewater Analysis (SMWW) [18]. The efficiency of the treatment was determined comparing the water quality parameters established in the Operating License (OL) of the Regulating Environmental Agency~~.~~

The sludge generated was submitted to sedimentation in the Imhoff Cone, vacuum filtered, dried at 60 °C in an oven and compacted. After this the dried sludge was then submitted to a pressure of 100 MPa, in a mechanical press.

The sludge generated in the treatment was analyzed qualitatively and quantitatively regarding the settled volume ASTM D3977 [19]; specific mass according to ASTM D854 [20]; moisture content ASTM D2216-10 [21]; ash, volatile matter and fixed carbon content (ASTM D3172-07) [22]; calorific value (ASTM D2015-00) [23]; elemental analysis USEPA 3051^{a} [24], USEPA 3050B [25] and ASTM D5373-02 [26]; and characterization regarding hazards according to the Standard NBR 10004 [27].

Finally, the following analysis were carried out: X-ray diffraction in a Siemens diffractometer model Kristalloflex D500; electronic scanning microscopy and elemental analysis by energy-dispersive spectroscopy (EDS) using a microscope model MEV EVO MA10 of the brand Carl Zeiss; granulometric analysis with laser beam diffraction ina in a CILAS 1180 Particle Size Analyzer; and thermogravimetric analysis in a Thermobalance Netzsch STA 409PC under oxidizing atmosphere (air).

Quantification of sludge considered average data of effluent generation by the company. The assessment of destination and recycling possibilities considered the regional and national contexts.

3 Results and Discussion

The results of the analysis of the raw and treated effluent deriving from the forging operation using water-based lubricant are presented in the Table 2. The raw effluent presents high concentration of suspended solids, organic charge in regarding DQO and DBO, total nitrogen and oils and greases. The value of 0.37 of the DQO/DBO relation 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, aluminum and boron. In general, the treatment presented high efficiency for suspended solids removal, which reflects in many water quality parameters. However, the effluent still presents concentration of DQO, DBO, soluble nitrogen and boron, which demands a subsequent step of treatment. This step is carried out at the company, in an aerated lagoon, and is not the objective of the present article.

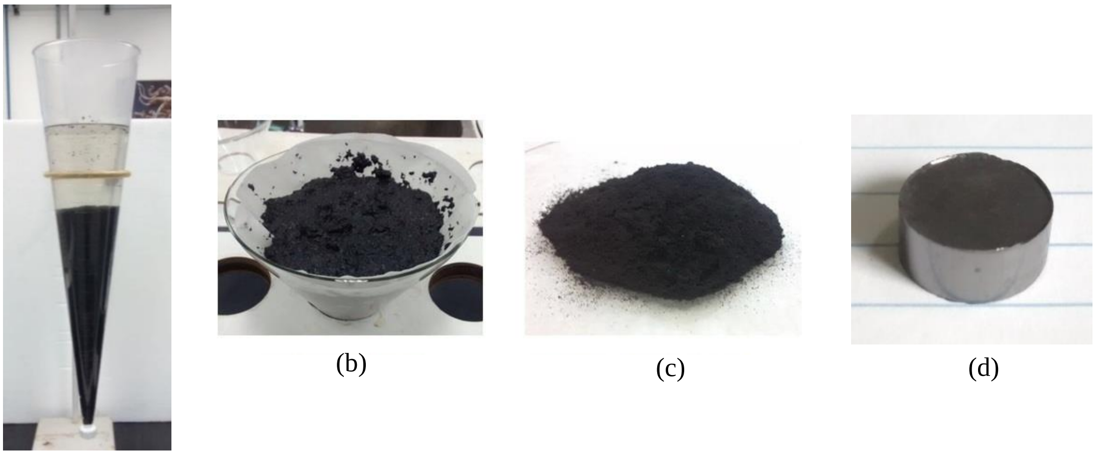
Table 2 - Parameters of the gross effluent treated with PAC and removal efficiency of the defined treatment

Parameter	**Effluent**		**OL Standard**	**Efficiency (%)**
	Raw	**Treated**		
DBO (mg/L)	6120	610	<= 110	90.0
DQO (mg/L)	16583	1650	<= 330	90.1
Total phosphorus (mg/L)	2	< LQ	<= 3.0	100
Total Kjeldahl nitrogen (mg/L)	295	160	<= 10	45.8
Suspended Solids (mg/L)	7870	12	<= 125	99.8
Sulfides (mg/L)	< LQ	< LQ	-	100*
Aluminum (mg/L)	163.1	0.188	-	99.9
Boron (mg/L)	50.6	39.2	<= 5.0	22.5
Lead (mg/L)	< LQ	0.102	-	***
Copper (mg/L)	1.25	0.093	<= 0.5	92.6
Iron (mg/L)	37.1	< LQ	<= 10	100*
Nickel (mg/L)	< LQ	0.017	<= 1.0	**
Zinc (mg/L)	1.35	< LQ	<= 2.0	100*
Oils and greases (mg/L)	300	< LQ	<= 10	100*
pH	9.63	6.40	6.0 – 9.0	-

* Measured value was below the quantification limit of the applied technique.

After the destabilization with 360 mg Al/L in the form of PAC and 25 mg/L of cationic polymer, the volume settled in the Imhoff Cone was measured. Sedimentation for 1 hour generated 450 mL of sludge per liter of effluent treated (55% of the volume of effluents in the clarified form) and when the period was extended to 24 hours, the volume was 400 mL (60% of the volume of effluent in the clarified form). The treatment with PAC generated a sludge mass of 17.1 g/L of effluent treated (1,7% m/V). As we can see, the sludge contains high amounts of water, which makes its disposal difficult and expensive. After the filtering process, the average content of solids reached 10.8% (m/V) for the PAC. Figure 2 illustrates the procedure, showing the sludge generated in the treatment process with PAC (a), after filtering (b), and after a step of drying in stove at 60 °C and clod breaking (c). Considering a monthly streamflow of effluent of 105 m^3/month and a generation, the mass of sludge to be managed is of approximately 30 t/month of filtered sludge.

It is assumed that this material is composed mainly by graphite and its characterization is important for a future destination.



(b) (c) (d)

(a)

Figure 2 - Settled sludge after treatment in the Imhoff Cone (a); after filtration (b), after drying at 60^{o}C and clod breaking (c); after compaction at 100 MPa (d).

Considering the dry sludge, it is present in the form of dust. The apparent specific mass of the material is 0.356 g/cm³. After the process of pressing at 100 MPa (Figure 2d), the material was consolidated and changed to a specific mass of 1.777 g/cm³, closer to the specific mass of pure graphite, which is 2.1 – 2.2 g/cm^3 [28-29]. This nearly 500% increase in the specific mass of the material suggests that the compaction of the sludge can be an alternative to decrease costs related to storage, transportation and disposal of this material, as the costs are related to the volume of material.

The dry sludge was observed in the electronic scan microscope, showing prevalence of flat particles in the granulometric range of few micrometers. The granulometric analysis conducted with laser beam diffraction indicates values of D_{10} of 1.9 µm, D_{50} of 5.9 mµ, D_{90}, 13.6 µm and D average of 7.0 µm. With the EDS analysis it was possible to identify the prevalent presence of carbon, iron and aluminum elements.

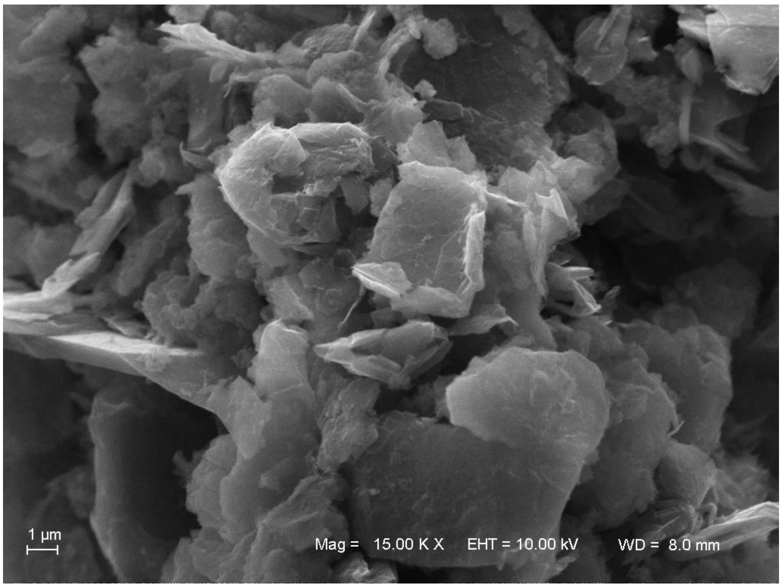


Figure 3 - Electronic scan microscopy image of graphite sludge deriving from the treatment of forging effluent employing water-based lubricant.

The results of the analysis regarding the classification according to NBR 10,004 show that the sludge of the forging effluent, water-based, when treated with PAC is classified as CLASS II A WASTE -

NON INERT. According to the standard, the sample did not present properties that give characteristics of corrosivity, reactivity, flammability, pathogenicity and toxicity.

The results of the elemental analysis of the sludge are presented in the Table 3. There is a carbon content of 70.7%, 4.8% of iron, 1.6% of aluminum and approximately 21% of oxygen. Other minor elements were found in very small amounts (less than 1%): sulphur, nitrogen, chlorides, fluorides, phosphorus, arsenic, boron, cadmium, calcium, lead, cobalt, copper, chrome, magnesium, manganese, mercury, nickel, potassium, silicon, sodium and zinc. The content of sulphur was 0.33% and of nitrogen was 0.21%.

Table 3 - Elemental analysis of the sludge generated in the treatment of the effluent of forging (using water-based lubricant) with PAC.

Element	**Amount (%)**
Carbon	70.73
Hydrogen	0.64
Nitrogen	0.21
Sulphur	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
Chrome	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
Minority Elements*	1.88
Total	100%

The diffractogram obtained with the DRX technique for the sludge with PAC is shown in Figure 4. Analyzing the diffractogram, it is possible to see that the prevalent crystalline species is graphite. The presence of a high intensity diffraction peak at 2ϴ of 26.56º, corresponding to the basal spacing of 0.335 nm, is characteristic of pure graphite. However, it was noticed a mild oxidation of graphite, which is demonstrated by the peak at 2ϴ of 10º [30].

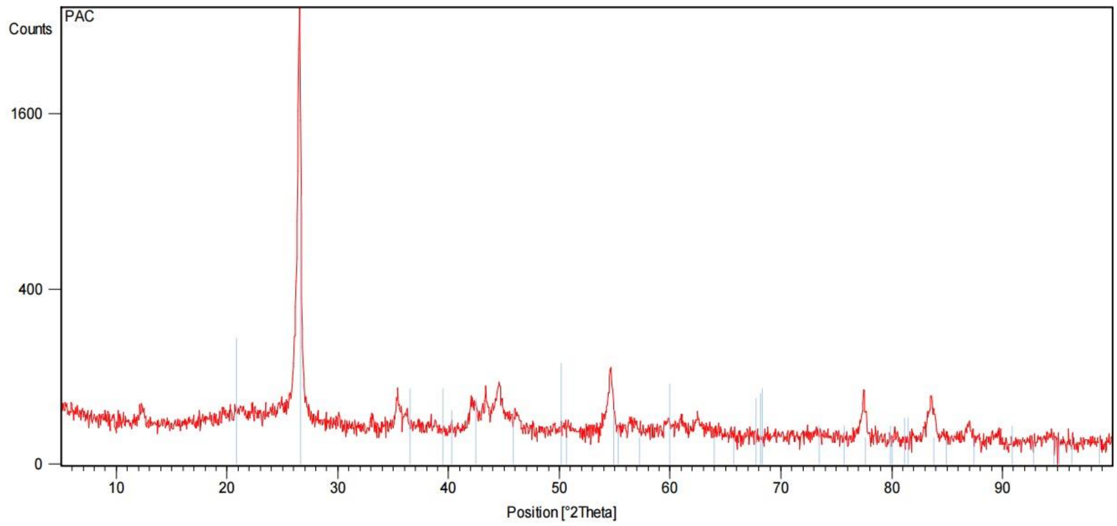


Figure 4 - Diffractogram referring to the DRX analysis of the sludge generated in the treatment of the effluent of forging (using water-based lubricant) with PAC.

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The sludge generated from the laboratory treatment of the forging effluent treated with PAC presents carbon content above 70%. The material is rich in graphite, which opens a range of possibilities for its destination, which might be in: 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 of the Company, there is a coal thermal electric power plant that could be a potential receiver of the waste.

Thus, the dry sludge was also submitted to immediate analysis and calorific value analysis (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 [31]. The high level of carbonification of the material associated with a moderate ash content resulted in a material with high calorific value (CV), of the order of 5850 cal/g. For comparison purposes, this material exceeds the specifications of the local thermoelectric plant, which burns coal with an ash content of 53%, a sulphur content between 0.8 and 1.3%, calorific value of 3,100 cal/g and 15% of moisture [32]. Other materials employed for power purposes in the region are eucalyptus sawdust (4145 cal/g) and rice husk ashes (3980 cal/g) [33-35].

Table 4 - Immediate analysis of the sludge generated in the treatment of the effluent of forging (using water-based lubricant) with PAC (dry basis).

	Water-based sludge
Calorific value (cal/g)	5850
Ashes (%)	21.4
Volatile matter (%)	9.0
Fixed carbon (%)	69.6

These results are confirmed by the thermogravimetric analysis, which enables analyzing the variation of the mass as a function of time and temperature (Figures 3). The test was carried out in oxidizing atmosphere until the temperature of 1000 °C. It is possible to see, in this figure, that significant loss of mass occurs only above the temperature of 600 °C. From 600 °C to 1000 °C, the sample loses more than 80% of its total mass, a typical behavior of thermal decomposition of most graphite materials [36].

The remaining mass of the sample deriving from the PAC treatment, approximately 19%, is similar to the ash analysis.

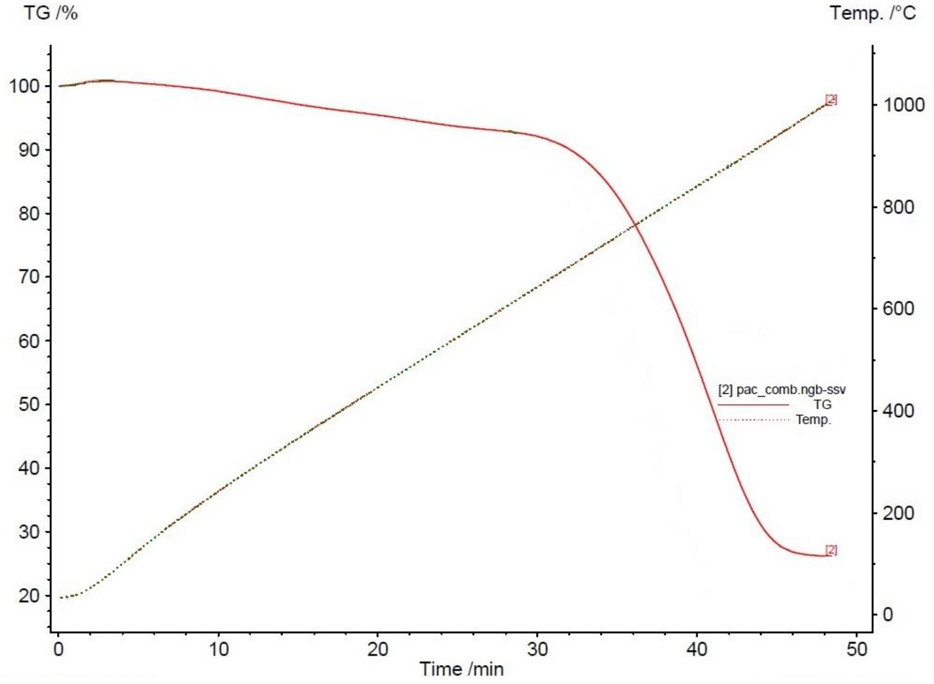

Figure 5 - Thermogravimetric analysis of the sludge generated in the treatment of the effluent of forging (using water-based lubricant) with PAC.

Thus, there has been as increase evolution of sludge management. The sludge originated in the past, with the wastewater treatment plant dealing with the water derived from oil-based lubricants, was transported without filtration to another state to be processed in cement kilns leading to high costs. The change in lubricants from oil-based do water-based simplified the water treatment process, and generated a sludge that can be filtered, dried and compacted, reducing storage, transportation and disposal costs. The characteristics of oil-free sludge allowed sending to cement kilns in the same state, reducing partially the costs of destination. However, after sludge characterization, other uses could be considered, including as co-fired combustible to coal thermal power plants. Perhaps, in a near future, it will be not necessary to have costs to discharge this sludge or, even better, to receive a payment. The forging sector, as a whole, seeks to find, not only the zero-waste destination in landfills, but markets that could increase opportunities to a proper destination of all waste materials of the productive chain.

4 Conclusions

Forging industries generate considerable amount of emissions, effluents and waste, requiring investments to prevent pollution and environmental damage. The treatment of effluents is a required operation. The use of water-based lubricants, replacing oil-based lubricants, improves the environmental performance. The change of lubricant enabled a sludge that can be easily filtered and handled. It presents a carbon content of 70% mainly in the form of graphite, with certain level of oxidation. In a regional context, it may be surely employed for power generating purposes in thermoelectric plants or cement kilns. However, other application alternatives are being investigated, including its cleansing and return to the lubrication process.

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