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WASTEWATER EFFLUENT GENERATED BY GROUT INDUSTRIES IN BRAZIL

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Abstract: Civil construction has grown inadvertently in Brazil, and, consequently, its demands for raw material. The production of such materials, as to any industrial process, yields wastewater effluents and has as destination, in general, water resources such as rivers and lakes. Nonetheless, government inspection cannot keep up with the number of starting companies, resulting in impunity due to lack of inspection. In the present work, the first of the kind, some chemical-physics aspects of wastewater effluents samples generated from grout industries were analyzed. The study shows that the pH of these samples lie outside the established limit by the national laws. The extremely alkaline pH and high conductivity of these effluents may cause severe damage to the aquatic environment in which they are disposed.

Keywords: Grout Industry; wastewater effluent; pH; electrical conductivity

INTRODUCTION

All around the world, aquatic ecosystem is used for various purposes. This ecosystem is one of the most threatened in the world, since they are ideal for human settlement and highly exploited to capture water for public supply and irrigation, to generate electricity and sewage disposal, among many other things. The quality of water used for domestic supply and biodiversity can be compromised as a result of pollution from various sources, such as domestic wastewater, industrial wastewater and superficial urban runoff and agricultural (Sperling, 1993; Marten & Minella, 2002; Malmgvist & Rundle, 2002). Regarding quality, the limnological conditions depend on the balance of several parameters. Among them, we highlight the pH (hydrogen potential) and the electrical conductivity, which should be in a certain range to ensure water quality. For example, high pH values can cause the death of fish and other marine animals (Wurts & Perschbacher, 1994).

In aquatic environments, pH values far from neutrality may affect the growth rates of microorganisms and acids pH encourages the proliferation of algae. Ideally, the pH for aquatic life should be situated between pH 7 and 8, wherein the fish are unable to survive in pH lower than four and higher than nine (Peixoto, 2007; Von Sperling, 2005; Weinstein, 1997).

Furthermore, high pH levels can change the toxicity of other pollutants already present in the water, as in the case of ammonia, which become more toxic in alkaline water, since the free ammonia (NH3) in the presence of a high pH ($pH > 8.5$) is more toxic to the aquatic ecosystem compared to its oxidized form (NH4 +) (Morrison *et al.*, 2001).

Another indicator of pollutants in aquatic environments is the electrical conductivity. This depends on ionic concentrations and temperature, indicating the water salinity. Thus, it is an indirect measure of the concentration of pollutants. Although there are no national laws in Brazil that set limits for conductivity, one can say that, in general, levels above 100 µS/cm can indicate environmental impact (Cetesb, 2009).

Furthermore, the presence of heavy metals can change the characteristics of the river. According to Brazilian Regulations, there is a certain amount of each heavy metal that is acceptable to be discharge at water bodies that will not change its characteristics. A high amount of heavy metals can pollute the rivers, and once it is polluted, fishes, surroundings, and even the fauna and vegetation that depend on this aquatic environment are going to be contaminated.

In industry, the use of water is essential and occurs in several ways: incorporation into the product and during the manufacturing process steps; water from the wash of machines, pipes and floors; sewage; to cool and steam generators, among other ways. With the exception of water that is incorporated into the product and the ones that are lost by evaporation; the remainder of water is contaminated by industrial process and originate liquid industrial effluents (Giordano, 2012).

The civil construction industry is one of the fastest growing in Brazil in the last fifteen years and with it, then has the demand for raw materials and services in this sector. The civil construction supply chain encompasses construction sectors ranging from the extraction of raw materials to the execution of the construction itself, being the sector that stands out for employment generation (John (2001)). Both wastewaters, from raw materials industrial processes for construction as the effluents from buildings, have a negative influence on the stream's water quality. Then, these wastewaters must be treated and channeled especially when they are dumped in areas where there is aquatic life (Mukhlisin *et al.*, 2012).

The mortar is one of the main construction's raw materials, and their production systems can be summarized as: mortar prepared at the construction, industrialized grout bags, industrialized mortar in silos and mortar dosed at central (ABCP, 2014).

The mortar dosed at central is seen as a way to rationalize materials, since, when one centralize all its production processes in a specialized industry, the construction eliminates the operations related to production control (receipt of raw materials, storage of raw materials, essays, cost of manufacture) thereby, reducing costs (ABCP, 2014; Lima *et al.*, 2003).

Like any other production process, the dosage of the mortar at central generates industrial wastewater that, most of the time has as final destination the water resources, by its direct disposal or by the public or industrial sewage collector system. It is worth noting that it is scarce the number of work papers which studies the wastewater of such industrial process.

On January 8, 1997, The Brazilian National Congress enacted the Law no. 9433 which established The National Water Resources Policy, and created the National System for Water Resources Management. The law, among others, aimed the creation of an Information System for Water Resources, seeking to gather and disclose qualitative and quantitative data of all National System for Water Resources Management, focusing on encouraging and controlling the industrial use of water and to meet the requirements of the hydraulic branch, by maintaining priority to economic development (Brazil, 1997; Soares, 2003).

In this sense, the aim of this work is to analyze, from the chemical-physics point of view, the quality of wastewater generated by mortar plants and check if this dump is in accordance with the national laws, and therefore check if it is appropriate for human consumption and marine life, through on-site studies of two central mortar located in Brazil. Four measurements are performed to quantify the wastewater: PH, conductivity, atomic absorption and Impedance spectroscopy. The results indicate that such wastewater is dangerous and should be looked upon more carefully by researchers and governmental agencies.

MATERIAL AND METHODS

Samples from two stations Mortar located in the south region of Brazil were analyzed. The production process of the visited plants has similar characteristics, but management and different layouts. In both cases, the companies responded to requests and inquiries made during a visit. The first mortar industry visited, here called CA1, has a national comprehensiveness, owning more than 10 units around the country and it provides wet industrialized mortar for important builders in the business of construction. The company has a fully automated process, and an environmental policy established.

Due to its environmental policy, the company has installed rainwater collection, aiming to use in cleaning the patio. Two tanks are intended for this purpose. The wastewater from its industrial process, as well as patio's washes, goes straight into a decanter which is located at the lowest point of the plant (**Fig. 1**). This decanter has the purpose of separating solid particles from liquid, since this water returns to the faucet to be used again for washing propose associated with the water reservoir rainwater.

The solid particles, which are composed primarily of sand and cement that were separated by sedimentation, are stored in a special area and shipped, still wet, for a recycling company where it will receive appropriate treatment before its final disposal.

Fig. 1 Wastewater decanting process of CA1.

It is important to note that part of the wastewater is taken, by the recycling company, associated with the solid particles. Thus, the company claims to have a closed cycle, where its industrial wastewater whether remains in the company or is sent for treatment, but it is never released to the environment.

The second company visited, called CA2, is a small mortar industry, which provides mortar for local and regional construction.

In this company, all effluent resulting from industrial process or patio's wash goes straight to a decanter before being dumped into the sewage collection system. **Figure 2** illustrates the decanter used by the company. This decantation process allows the separation of solid particles from the liquid before its final destination. The company has no environmental policy.

At the CA1, one sample was collected and at CA2, four samples were taken in different days. In both companies, samples of the input and output of the decanter were taken to check pH, electrical conductivity, impedance spectroscopy and atomic absorption spectroscopy.

Samples of both central mortars were analyzed by a pH meter Model HSP-PHTEK 3B to check its pH level.

The electrical conductivity tests were performed in a laboratory of Analytical Chemistry using a conductivity model TECNOPON mCA-150. The impedance spectroscopy was made with Impedance/Gain – Phase Analyzer SI 1260 – Solatron.

Last but not least, the samples were analyzed to check the presence of heavy metals such as: Cadmium (Cd), copper (Cu), nickel (Ni), chromium (Cr), lead (Pb), since such heavy metals are hazardous to man and the nature, and calcium (Ca) that must be abundant in samples of this type. These analyzes were performed by using an atomic absorption spectrophotometer Varian AA 175 model.

Fig. 2 Decanting system for wastewater of CA2.

pH

CONAMA (National Environmental Council) Resolution No. 20, of June 18, 1986, classified Brazilian waters in freshwater (salinity <0.05%), brackish (salinity between 0.05% and 3 %) and saline (salinity> 3%). Furthermore, the resolution was renumbered as the main Brazilian legislation to control water pollution, since it establishes parameters for the wastewater discharge into water bodies. This resolution was revoked by Resolution CONAMA No. 357/2005 which dispose about the classification of water bodies and environmental guidelines for its framework, and establishes conditions and standards for wastewater discharge, and other measures; this Resolution, on the other hand, was subsequently amended by Resolutions No. 370/2006, no. 397/2008 , no. 430/2011 and no. 410/2009.

CONAMA Resolution 430, of May 13, 2011, which is still valid, provides conditions and standards for wastewater discharge, and it is the most current CONAMA legislation to establish parameters and conditions for wastewater discharge in the body receptor. The law states in its article 16 that "any wastewater coming from a polluting source may only be released directly into the receiving water body if they satisfy the conditions and standards set in this article" which states that the pH should be between 5–9.

In addition to the samples collected, a sample of distilled water was analyzed aiming to serve as a standard in comparing the results. The values obtained for the PH are shown in **Table 1**.

Table 1. pH results

Sample	pH				
	CA1	CA2			
		1	2	3	4
Distillated	7.5	7.5	7.5	7.5	7.5

water					
Decanter entrance	13.7	12.3	13.0	12.1	12.4
Decanter exit	13.5	12.2	12.6	9.5	12.2

Different from the sample of distilled water, all other samples showed extremely high pHs, which are harmful to humans and especially to aquatic resources.

The most abundant compound in the mortar is cement. The cement contains more than 67% of CaO (Calcium Oxide). The CaO, when in aqueous solution, forms calcium hydroxide (CaOH2) (Taylor, 1990). Therefore, it is reasonable to assign this high alkalinity of the samples to the presence of calcium hydroxide. The alkalinity observed in the samples is very high (similar dissociation of caustic soda in water) and can cause serious health damage (such as burns), plus, it can make aquatic life in rivers impossible if it is accidentally discharged on it.

In both cases, at the entrance of the decanter, the water remains still, then the sand can be decanted, resulting in a high pH due to the high concentration of elements present. In the decanting process, the basic elements, such as sand, are separated, either by settling or by direct absorption of larger particles. The decantation process can lower the pH, which results in a higher pH at the entrance than in the exit of the decanter. In addition, the decanting process seeks to remove sand, which is responsible for most of the dissolution of SiO2, which is the second most abundant compound in the cement, also known for its high alkalinity.

According to NBR 9800/1987, which establishes criteria for release of industrial wastewater into public sanitary sewerage collection systems, the permissible values for these effluent pH is between 6 to 10. The CONAMA Resolution no. 430/2011, in turn, admits values between five to nine for the pH of wastewaters discharged into water bodies. Then, based on both laws, if the wastewater final destination of both mortar industries were the sanitary sewerage or a water body, it is essential to treat it before dumping.

Electrical Conductivity

In addition to pH, it was also analyzed the electrical conductivity present in the samples. In **Table 2** are listed the values obtained with the assay.

Table 2. Electrical Conductivity Results

Sample	Conductivity (μS/cm)				
	CA1	CA2			
		1	2	3	4
Destilated water	13	13	13	13	13
Decanter entrance	9,850	8,670	8,220	1,280	2,490
Decanter exit	5,270	7,890	7,776	198	1,962

With the exception of distilled water, all other samples showed very high electrical conductivity. By simple comparison, we can see that it is 1000 to 10 000 times higher than distilled water, which can indicate a much greater amount of ions present in the environment.

However, this high electrical conductivity is likely due to the high concentration of calcium hydroxide and silicon dioxide present in the samples, as described before. As suggested by Horbe & Olive (2008), the calcium hydroxide and silicon dioxide can provide high levels of conductivity when dissolved in water.

Impedance Spectrum

In addition, the impedance spectrum experiment was done. It was analyzed the real and imaginary graphs to check with the dielectric properties of the samples.

The results of the impedance spectroscopy experiment concerning CA1 and CA2 are described in **Table 3**. The results of impedance analysis for the samples collected at CA2 were suppressed for the sake of space, since the tests showed only a relative change in resistance, confirming the conductivity, but no qualitative changes in the curves, in other words, the main mechanism presented between one measure and the other remained the same, only the amount changed.

The results for the decanter entrance's sample for both stations are shown in **Figs 3** and **4**. The first thing one notes is the fact that the real part has very low plateau, indicating very low electrical resistance. The results are in agreement with what has been measured by conductivity. Notice that in the case of CA2, the resistance is slightly higher than that in CA1, indicating a lower amount of ions. However, the maximum dissipation that occurs on the imaginary part is in the same frequency region for CA1 and CA2, indicating that these leaded elements are responsible for the spectra.

Table 3. Impedance Spectrum Results

Sample	Resistance (Ω)		Capacitance (pf)	
	CA1	CA2	CA1	CA2
Decanter entrance	8.00	11.83	2.80	1.19
Decanter exist	4.90	7.04	3.70	1.68

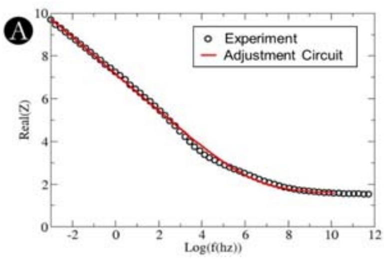

Fig. 3 Real and imaginary part of impedance spectroscopy to sample of decanter entrance for CA1. The circles represent the experimental data and the solid line shows the circuit fit.

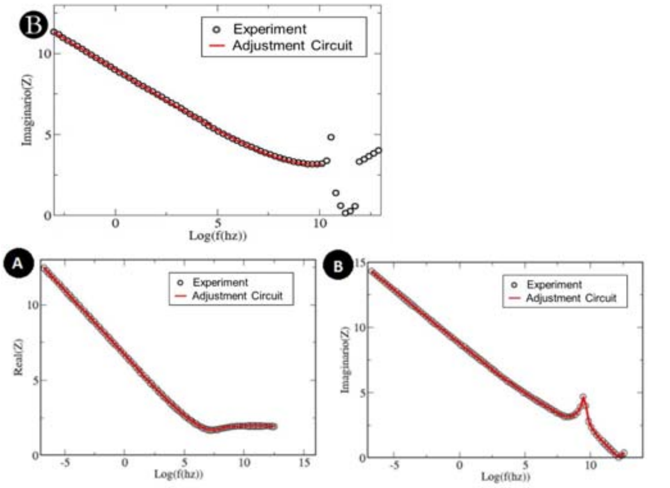

Fig. 4 Real and imaginary part of impedance spectroscopy to sample of decanter entrance for CA2. The circles represent the experimental data and the solid line shows the circuit fit.

The results for decanter exit samples, for both industries appear in **Figs 5** and **6**. As showed at the conductivity experiment, the resistance at the decanter exit is higher. This means that the decanter was able to remove a portion of these ions. However, the change is not significant, indicating that the function of the decanter for both companies is to decant and remove solids particles from the wastewater, but it plays no significant role in the treatment of the effluent. Just as at the entrance of the decanter, the two imaginary curves (**Figs 5b** and **6b**) keeps the dissipation peak in the same region, supporting the hypothesis that the ions present in the entry are still mostly in the decanter exist.

The results so far indicate that the analyzed water is harmful to both, human consumption and for nature. However, it shows no evident remnant of materials that is difficult to eliminate.

As a final test, the samples were subjected to analysis by atomic absorption spectrometry for the presence of hazardous elements like heavy metals. The presence of cadmium (Cd), Copper (Cu), Nickel (Ni),

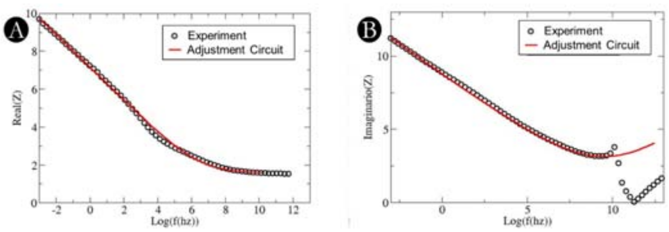

Fig. 5 Real and imaginary part of impedance spectroscopy to sample of decanter exit for CA1. The circles represent the experimental data and the solid line shows the circuit fit.

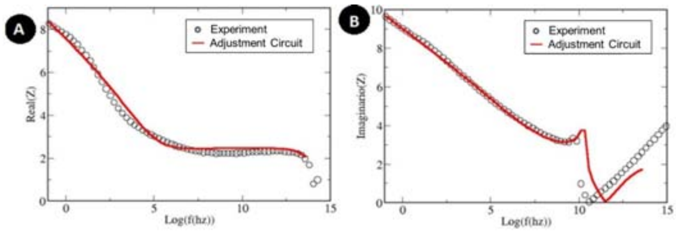

Fig. 6 Real and imaginary part of impedance spectroscopy to sample of decanter exit for CA2. The circles represent the experimental data and the solid line shows the circuit fit.

Table 4. Comparison of results for CA1 with the parameters established by NBR 9800:1987 and by CONAMA 430:2005

Sample	Obtained Values (mg.L^{-1})					
	Cd	Cu	Ni	Cr	Pb	Ca
Decanter entrance	0.001	0.063	0.043	nd*	0.147	20.68
Decanter exit	0.008	0.611	0.015	0.021	0.143	22.13
NBR 9800:1987	0.1	1.5	2.0	5.0	1.5	-
CONAMA 430:2005	0.2	1.0	2.0	0.1	0.5	-

nd* - concentration bellow machine's lower limit

Table 5. Comparison of results for CA2 with the parameters established by NBR 9800:1987 and by CONAMA 430:2005

	Sample	Obtained Values (mg.L^{-1})					
		Cd	Cu	Ni	Cr	Pb	Ca
Sample 1	Decanter entrance	nd*	0.07	nd*	nd*	0.80	997.40
	Decanter exit	nd*	0.61	nd*	nd*	nd*	460.40
Sample 2	Decanter entrance	0.02	0.02	nd*	0.06	0.40	621.43
	Decanter exit	0.02	0.04	nd*	0.12	0.31	533.83
Sample 3	Decanter entrance	nd*	nd*	nd*	nd*	nd*	92.22
	Decanter exit	nd*	nd*	nd*	nd*	nd*	8.90
Sample 4	Decanter entrance	0.01	nd*	nd*	nd*	0.09	193.29
	Decanter exit	0.01	nd*	nd*	nd*	0.06	153.71
	NBR 9800:1987	0.1	1.5	2.0	5.0	1.5	-
	CONAMA 430:2005	0.2	1.0	2.0	0.1	0.5	-

nd* - concentration bellow machine´s lower limit

chromium (Cr), Lead (Pb) and Calcium (Ca) elements were investigated.

At **Tables 4** and **5,** one can see the results obtained by atomic absorption spectrometry for the CA1 and CA2 respectively, compared to the maximum parameters established by NBR 9800:1987 and by

CONAMA Resolution 430:2005 to the release of industrial wastewater.

As can be observed, though a small amount, all metals were found in the CA1, unlike CA2 where elements such as cadmium, nickel and chromium are not present in detectable levels. Moreover, it is important to note that in the sample 3 for CA2, with exception of calcium, all the other elements were not detected in any stage of the process. This is due to the fact the company had cleaned the decanter the day before the sample was collected. Thus, it is inferred that if the decanter were cleaned, at certain intervals to be determined by future studies, it would be more efficient in the process of removal of heavy metals. Calcium, as might be expected, was the only element with high amounts found in the samples for both companies. Regarding the laws analyzed, no chemical element analyzed overcomes the limits, allowing us to conclude that there is no need to treat the effluent to reduce or eliminate these elements. It is worth noting, however, that besides the fact that some values are lower than what is established in the resolution, they are close to the limit, such as Cu at the decanter exit to CA1. This does not ensure that all the wastewater is below the certified by law for these materials, and does not extinguish the possibility that, if the wastewater is being released over a long period of time in a river or soil it is not making them unsuitable, which should be checked with a deeper study. However, the use of a decanter for removing calcium, for example, which occurred in the CA1 and CA2 showed that the use of only the decanter can be inefficient in wastewater treatment being effective only in the removal of solid particles present in it.

CONCLUSIONS

The research has shown that the effluents generated by both mortar industries analyzed do not respect the upper limits established by Brazilian legislation with regard to pH, being the effluent even after decanting, extremely alkaline. Still, with regard to the presence of metals in the effluent, the CA2 showed no significant results. While CA1, although it did not have heavy metals in amounts non-standard, showed that many values are relatively close to the maximum allowed. In the case of CA1, even with the high alkalinity of pH, there is no river pollution, since, according to the company, the effluent is completely reused or recycled within the company, thus fulfilling the standards set by the country's law. However, the CA2 dumps their wastewater directly into water bodies and it must have to prioritize their effluent treatment especially with regard to alkaline pH, neutralizing it before the release in the water body.

Furthermore, it can be inferred that cleaning the decanter frequently can contribute to more efficient effluent treatment, as well as in the removal of metals as in the neutralization of the pH. However, the use of sedimentation to remove the elements when its pH concentration is high shows that the use of decanter may be ineffective in the wastewater treatment, being effective only in the removal of solid particles present in it.

The lack of supervision and the fear of companies to collaborate with research like this makes one consider that this can be a very common scenario, and several companies in the civil construction sector throw their effluents in small or large quantities in the sewage collection or water bodies with non-stander pH and with metals that can adversely affect aquatic life and humans. Often pollution occurs even due to lack of knowledge of the company in relation to legislation and the content of their effluent, which does not pass through specific studies or analyzes. The best solution to this problem would intensify inspection aiming the reduction of the number of companies that do not adequately treat their wastewater before final disposal.

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