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PROCESS WATER TREATMENT IN A THERMAL POWER PLANT: CHARACTERISTICS AND SEDIMENT/SLUDGE DISPOSAL

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Abstract

The industrial water quality of a thermal power plant is of high importance, and a process water treatment station being always required. Whatever the adopted treatment system is, it is accompanied by the production of different amounts of sediment and sludge, which must be disposed and valorized. This paper presents in detail, the physical-chemical treatment system applied for the industrial water production in a Romanian thermal power plant (Veolia Energy Iasi Co.), referring to its installations, performance achieved, and also the quality characteristics of the treated industrial process water and certain types of produced sludges (i.e. primary and desulfurization ones).

The industrial water treatment performance is very good (85-100%) in terms of suspended solids, turbidity, organics (expressed by COD), fixed residues, heavy metals content, total hardness and microbiological inhibitors. The water and total iron contents were high in the primary sludge and, for the desulfurization sludge, low water and moderate calcium contents were found to be present. Information on the applied treatment and valorization possibilities of primary sediment and sludge are recommended, all being dependent on the operational and maintenance costs of used conditioning and dehydration installations. The final result can be a newly added-value byproduct which would be used as raw or auxiliary material (uniform compact plates), but also the minimization of produced sludge amounts in association with the environment protection and the control of environmental pollution due to industrial water treatment station functioning.

Key words: ferrous salts-based coagulation, industrial water softening, process water treatment, sediment/sludge thickening, thermal power plant

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1. Introduction

Any thermal power generation is not a fully effective process in terms of environmental impact due to its by-products and wastes produced (gaseous, liquid-gas and solid ones), among others. In the energy sector, a conventional thermal power plant is based on the combustion of a ‘clean’ fossil fuel to produce steam and/or hot water for different industrial and domestic utilizations by using different installations/systems, e.g. transport/transfer

installations, fuel preparation and storage systems, combustion installations, water supply systems, process water treatment stations, wastewater treatment systems, or neutralization systems, sewage systems, disposal platforms of slag, ashes and by-products of neutralization processes etc.

Process water, depending on its origin, can contain a wide range of dissolved substances or/and suspended solids, being well known that water is commonly a very good solvent. Therefore, as one of important raw matter, industrial water is usually

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treated in a station to obtain the quality required as process water in a thermal power plant, considering its principal scope of useful and safe thermal energy production and its efficient distribution, conversion and consumption by all interconnected industrial, public and domestic consumers.

The treated water will be used as process water or industrial water in the water-steam and/or water-water circuits of the thermal power plant where can be impurified due to the dissolved chemicals, formed precipitates and agglomerates, as well as residual chemicals caused of evaporation, cooling and heating processes in different thermal installations, etc.

Process water can be used as *additional process water* (with very low content of salts and gases), requiring pre-treatment by mechanical (filtration, sedimentation), chemical (carbonation by absorption with lime, coagulation, ionic exchange) and physical (thermal degasifying, vaporization, boiler stripping) methods, and as *cooling water* (with as low as possible temperature) after a corresponding treatment (especially water softening or demineralization).

Therefore, the main aim of a process water treatment station in a thermal power plant consists in the production of industrial water with adequate characteristics for specific use in order to ensure a safe and long time period exploitation of thermo-energetic installations and connected systems from the water-steam, or water-water circuits, meaning those used in:

(i) The chemical degasifying station (i.e. carbonation and desulfurization processes by absorption of CO₂ and SO₂ gases in alkaline/lime solution followed by mechanical filtration);

(ii) The primary process water treatment station (coagulation-sedimentation);

(iii) The industrial water softening station (hardness reduction by ionic exchange process), but also the treatment, disposal and valorisation (when is possible) of primary and desulfurization sludges separated from the industrial water treatment stations in association or not with other technological process steps.

The implementation of 'circular economy' concept in the thermal power plant implies an increasing interest for individual, or even 'in mixture' treatment and valorization of its by-products and wastes for new raw matter or auxiliary/conditioning material preparation with certain added-value, chemical reagents solution preparation, or uses of hybrid thermal power systems (conventionally associated with renewable ones) which will minimize and control the environmental impact and potential risks, among others (Bangviwat and Sakda, 2018; Fabian et al., 2016; Grigore et al., 2016; Sposato et al., 2017; Zivkovic et al., 2018). Therefore, the process water treatment system would be continuously improved and its produced sediment and sludge treated and completely valorized (Ahmadi et al., 2013; <http://purebalticsea.eu>; <http://veoliawatertechnologies.co.za>).

That is why this work is focused on the in-detail presentation, for the first time, of the case study of Veolia Energie Iasi Company, a Romanian thermal power plant, especially considering the following important key elements of the industrial water treatment system:

- The principle characteristics of the existing industrial water treatment stations, discussed mainly considering (i) the required process water quality; (ii) the industrial water treatment system and its performance, and (iii) the existing facilities and its required improvements;

- The primary sludge characterisation produced in the primary water treatment station and also the characteristics of the sludge formed in other technological steps (Zaharia, 2015; Zaharia, 2018; Zaharia and Suteu, 2013), mainly in the flue gas desulfurization step, referring to some physical-chemical quality indicators of the primary and desulfuration sludges;

- The disposal and valorization possibilities of the primary sludge and other sludges separated from the industrial water treatment steps, individually and in mixture with different solid waste produced in the technological process of solid fossil fuel combustion in the studied thermal power plant (e.g., slag, bottom and fly ashes, neutralization waste), as raw materials or auxiliary/conditioning materials with new added-value, possible to be used in the preparation/synthesis of new adsorbents, coagulants, geotextiles, synthetic fibers or stabilized composite products) (Harja et al., 2009; Niculita et al., 2017; Singh et al., 2016; Serbanoiu et al., 2017; Sua-Iam and Makul, 2017; Yuyou et al., 2016; Wang et al., 2017).

2. Experimental

2. 1. Short presentation and location of the studied Romanian thermal power plant

The investigated Romanian thermal power plant is owned by Veolia Energie Iasi Company and is located on the platform of a former heat and power co-generation plant (CET Electrica Iasi Co.), and composed actually of two thermal energy stations: (1) *a thermal power station* (named CET 2), working based on a 'clean' solid fossil fuel i.e. processed superior coal - huile (washed and treated with specific chemicals for impurities removal) which is oxidized rapidly (exothermic steps, its chemical potential energy is transformed into thermal energy – 140 Gcal produced by combustion of 140,000 tons of huile for six months) by the oxidant (O₂/air) and uses significantly high quantity of industrial process water which must be permanently treated and added in the closed water-steam or water-water circuits (two boiling systems CPG-42 steam boilers of 420 t/h), normally operating only in the cold season (November – April), and (2) *a process water boiling station* (named CET 1), working with an ecological gaseous fossil fuel, i.e. methane gas, used only for hot water production (one boiler of 80 Gcal/h) in the hot season

(May – September), meaning around 20 Gcal of thermal energy produced by using 9 million Nm³ of methane gas during 6 months, which requires also significant quantity of industrial water which must be continuously treated and added in the closed thermal circuits.

The fresh industrial water for CET 1 and CET 2 thermal power stations is supplied by ApaVital Iasi Company, as *industrial* and/or *potable water*, and a huge amount of recyclable industrial water (after a corresponding mechanical – physical-chemical treatment) is used, too (recycles up to 80-90% of water used in the company, the rest being lost in the technological process of thermal energy production).

This Romanian thermal power plant is located in the industrial area of one of the most important historical, economic and cultural centers of Moldavia region, one of the oldest cities in Romania, Iasi municipality (371,889 inhabitants). A few residential zones are nearly the company site and separated by permanent surface water (i.e. Bahlui River, having a mean flowrate of 0.189 m/s, a mean shape of 5.3 %, and an annual flow of 2.16 m³/s in Iasi county area) (Zaharia and Surpateanu, 2006), that is why the prevention, reduction and control of environmental pollution produced by all activities onto emplacement of this studied Romanian power plant is one of significant company concerns/issues and also imposed legal obligation.

The most important facilities of this studied thermal power plant are divided as follows: an industrial water supply system, a solid and gaseous combustion fuel station, a steam and hot water generation system (with certain important principal and secondary thermal circuits), and an electric energy transformation and transmission system to/from the National Energy System (NES) (Stanciulescu, 2004; Zaharia and Surpateanu, 2006). The thermal power plant is an important consumer of water (i.e. industrial process water as demineralized, or soft water, or cooling water, but also drinking water for its employee's needs) (Zaharia, 2006), that must be permanently treated for adequate use as process water in the thermal energy production, distribution and consumption by local population and all institutes and companies connected to the municipality heating system.

2.2. Industrial water treatment stations: materials, chemical reagents, analysis methods used and schematic treatment flux description

The principal materials and chemicals used in the industrial water treatment stations are grouped as follows (Stanciulescu, 2004; Zaharia, 2006):

(i) *Lime and ferrous sulfate-based coagulants*, used in the industrial water treatment step, as:

- *Lime*, in hydrated powder form, corresponding to SR EN 459-1:2003 standard (EN 459-1 CL 90-s) with the following characteristics: min. 80–90% total sum of CaO and MgO; 3-5% MnO; 4-7% CO₂; 2% SO₃; apparent density of 0.3–0.6 kg/dm³;

max.7% R009; max. 2% R020; 2% free water; the stability test is adequate. It is stocked in three cylindrical metallic tins fixed with 4 arms on the industrial cement concrete platform (each one possessing a superior lid with three covered adapters and a conic bottom with a discharging hole on which is mounted the dosing installation of powder lime). It is used as lime solution for the industrial water treatment station, prepared by dosing of a specific lime amount and dissolved it with water till a homogeneous lime solution preparation in each consumption tank (cylindrical tank of 2 m³, diameter of 2.2 m, and useful height of 2.2 m) using a dosing pump (Rotosole, flowrate of 10 m³/h, 10 m CA, 2.2 kW, 3,000 rot/min, for 0-300 kg of powder lime/h) and ejecting pump (flowrate of 20 m³/h, 4.5-5 kgf/cm², 55 m CA, 17 kW, 2,950 rot/min) for gravity settling tank supply.

- *Ferrous sulfate*, in hydrated solid form of FeSO₄·7H₂O, as residual product from iron (and steel) works (Galati), resulting by dissolution of steel rests from different mechanical processing, with the following characteristics: microcrystals of greenish color, purity of 97.5% for Ist class and 95% for IInd class, and solubility of 99.8 %. It is stocked in specific deposit with two discharging holes and a supplying source for coagulated water in which is dissolved ferrous sulfate in two preparation-dissolution tanks and after introduced in the underground consumption tanks. These consumption tanks dispose of mechanical agitation system, being supplied from four dosing pumps (*two* of PVC type, with flowrate of 0-0.6 m³/h, 25 m CA, 2.2 kW, 1,425 rot/min, and *two* of Dorel 320 type, ICPEET Cluj, with flowrate of 0-0.6 m³/h, 50 m CA, 2.2 kW, 1,425 rot/min) and discharged in the primary settling tank. Ferrous sulfate is the *coagulation agent* and reacts in the primary settler with the lime solution forming the ferrous and ferric hydroxide as precipitates in high volume which agglomerate and retain in settling, the fine solids in colloidal range as well as specific adsorbed organics and not used / remanent microbiological inhibitors. The ferrous sulfate consumption tank is a cylindrical metallic tank with internal protection by surface rubbering (4 m³, diameter of 2 m, liquid height of 1.4 m and total height of 2.2 m) equipped with three steel holes at inferior bottom for emptying, outlet of ferrous sulfate solution (Dn 80) and inlet of compressed air (Dn 50) and a lateral hole (Dn 50) for recycling of ferrous sulfate solution.

(ii) *Compressed air* – the compressed air system (EC10, 6 kgf/cm², temperature range of -25 ÷ 40°C, 2 compressing steps, 4 cylinders, 10 L-oil bath, regulatory rotation of 900 rot/min, minimal operating rotation of 400 rot/min, (10 atm)-flowrate of 5 m³/min, 52 kW) is composed of a recipient of 1 m³ (or 16 m³) capacity, a drops separator and a dryer with silicagel, which continues in a distribution unit with 4 holes with valves and a gas gauge. It is required in the mechanical filtration, pneumatic discharging of powder lime from transport machines in tins and also lime solution preparation and supplying of primary settling tank for normal operation and fluidization, when is necessary.

(iii) Sulfuric acid, hydrochloric acid and sodium hydroxide – for the neutralization processes (concentrated and diluted working solutions) and salt solution (7-10 % NaCl, flowrate of 25 m³/h, 9000 L- total consumption of 25% NaCl solution for an active cycle) for regeneration of ion exchange materials;

(iv) Ammonia, hydrazine and sodium phosphate solution– for water conditioning in water-steam circuit, used when is required;

(v) Silting and erosion inhibitors, chlorine and sulphuric acid – for cooling water conditioning, and

(vi) Polymer (mixed anionic and cationic polyelectrolytes), as commercial product (concentrated solution, 35-40 %) (only when is required, for no significant supplementary added cost) – for primary and ‘in mixture’ sludge concentration and its valorization after mechanical dehydration (by simple gravity thickening or gravity belt thickening).

A number of other chemicals, e.g. acids, alkalis and organic compounds, are used for maintenance of existing installations and equipments, and others are required in the permanent analysis of the most significant physical-chemical quality indicators of industrial water (suspended solids, dissolved oxygen, chlorides, COD, or COT, total hardness, content of calcium, magnesium, sodium, carbonates, ammonia, phosphates, extractible substances, certain specific anions, etc.) using international approved analysis standard methods (Zaharia and Surpateanu, 2006; Zaharia, 2014, 2018). From the whole industrial

process water treatment station, it is produced the predominant inorganic primary sludge which is pumped and separated in a simple gravity thickening basin (4 compartments-based basins for sludge concentration and separation (iron-based hydroxide precipitates or co-precipitates associated with other separated aggregates or colloids) and, in a few cases, in a gravity belt thickener which uses a polymer to make sludge particles larger to be well separated.

The general scheme of the industrial water technological treatment plant is illustrated in Fig. 1, in the form received from the company responsible staff (in Romanian).

3. Results and discussions

3.1. Industrial water treatment processes and specific systems: mechanisms and performance

The industrial water treatment involves the removal from raw or loaded industrial water of constituents detrimental to specific use (addition or cooling water, hot water). Industrial water supplies must be nearly sterile and turbidity-free and should have a very low total dissolved solids concentration (as total dissolved salts, or fixed residues at 105°C) (Haller, 1977; Zaharia, 2006, 2014). Specific chemical species such as hardness ions (calcium and magnesium ions), or specific metal ions such as iron species, and organics must be removed in the majority of cases.

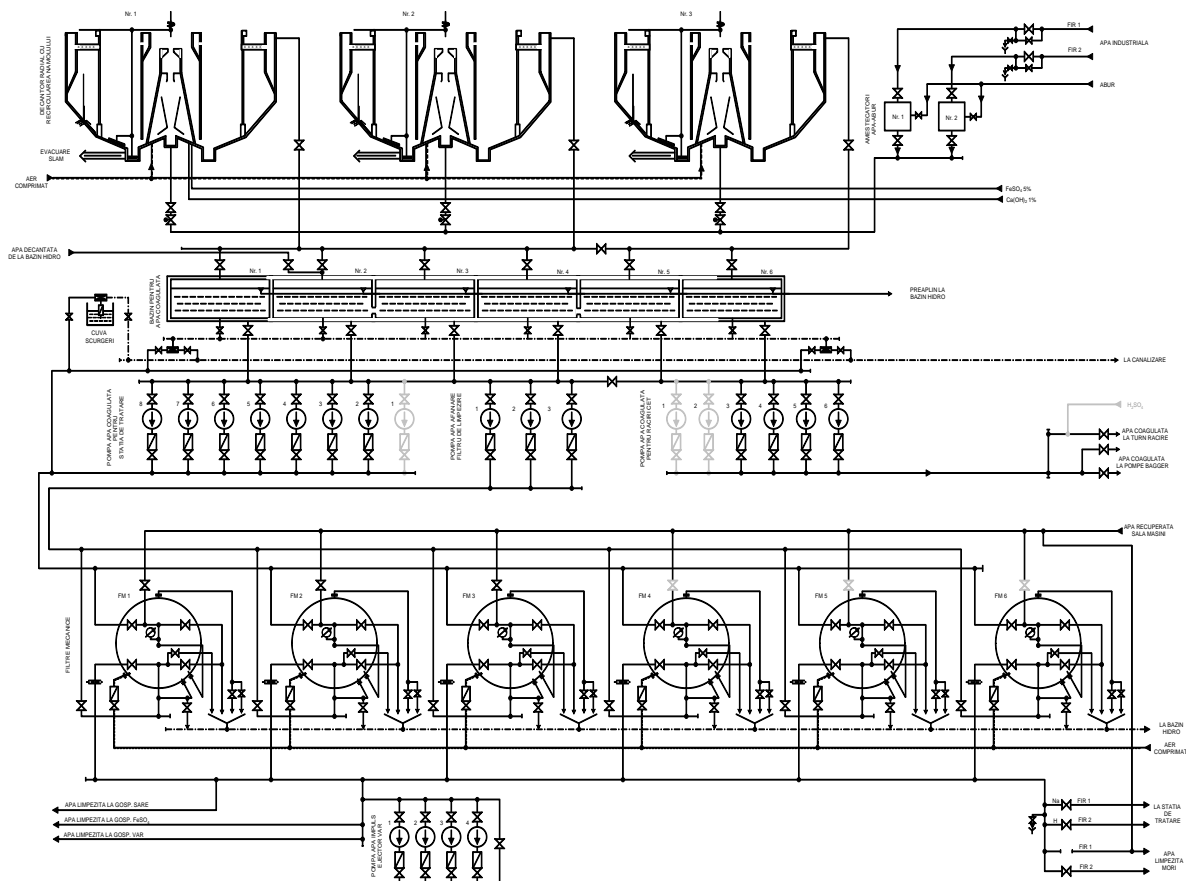


Fig. 1. Schematic representation of the industrial water treatment plant (Veolia Energie Iasi Co.)

Requirements for industrial uses of water vary widely, from (i) *cooling* which has a relatively loose requirements (corrosion, scale formation, bacterial growth in pipes and cooling towers as primary concerns) to (ii) *boiler feed water supply* (working at high temperature and pressure) which has a major problem with scale formation, and a particular one with silica, that is why boiler feed water must be very low in turbidity (no more than 0.05-0.1 FTU), dissolved oxygen (< 2 mg O₂/L; the imposed ISCIR norm (ISCIR – State Inspection for Boilers, Under Pressure Recipients and Lifting Installations (www.iscir.ro) is of 0.02 mg O₂/L), total iron content (<0.1 mg/L) and total hardness (zero value is recommended).

Consequently, industrial water quality is a significant concern in such cases, and requires mechanical-physical and chemical treatment by specific common processes and operations such as *coagulation-sedimentation* for turbidity removal, *precipitation and ion exchange* for dissolved solids and total hardness removals (i.e. hardness removal by precipitation and ion exchange, and also iron removal by oxidation and precipitation to insoluble trivalent form), or *disinfection* by *chlorination* (easy operation and low cost) in cooling towers, pipes and mechanical systems for prevention or control of slime growth. Thus, the industrial water treatment should be organized on well-defined treatment steps, such as *pretreatment* (with lime for the elimination of CO₂ and SO₂) followed by *primary treatment* and *softening* which are characterized as mechanism, specific installations and performance in further sections.

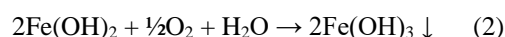
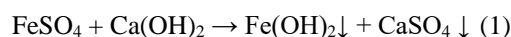
3.1.1. Primary industrial water treatment processes and specific systems

The primary industrial water treatment step consists in coagulation of fine suspended particles of colloidal range normally carried out prior to sedimentation and filtration steps, associated or not with the chemical degasifying process (CO₂ and SO₂ elimination with lime by carbonation and desulfurization followed by mechanical filtration) and reduction of total hardness (reduction of Ca²⁺ and Mg²⁺ ions in treated industrial water by precipitation as carbonates in gas-water-solid equilibrium situations, or by lime-soda softening process closed to the atmosphere but open to the solid precipitation/scale formation). Usually coagulants (lime and ferrous sulfate) are added to industrial water and rapidly agitated for a few minutes to disperse, and after gently mixed for 15-30 min for flocs' formation (precipitated agglomerates as flocs). When only slower mixing rates are used, higher coagulant dosages may be necessary due to the range of metal-complex species produced. At high mixing rates, the increased surface area produced by particle disintegration increases coagulant dosage requirements. Data on suspended solids, residual turbidity, total hardness, permanent acidity and alkalinity should be measured as a function of

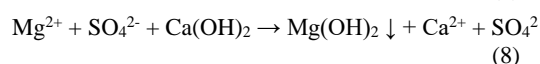
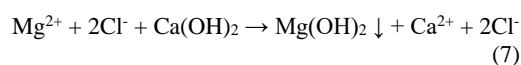
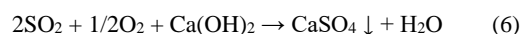
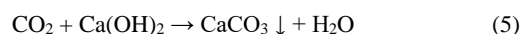
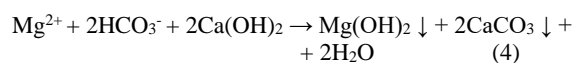
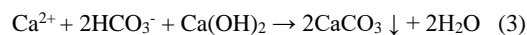
coagulant dosage, pH, Reynolds number and temperature.

When ferrous sulfate is used in water treatment devoid of oxygen, the pH must be higher than 9.5, effect achieved by the addition of lime solution (Eq. 1). However, when oxygen is present, the ferrous sulfate is oxidized to ferric hydroxide (Eq. 2), which is more insoluble than ferrous hydroxide (Haller, 1977; Yen, 2007).

Ferrous sulfate is transformed in precipitate which will coagulate all suspensions. In this manner, ferrous sulfate is used as a coagulant when oxygen is sufficient (Eqs. 1-2).



It can be also performed the partial reduction of water hardness, silica and CO₂ (even SO₂) elimination as in Eqs. (3-9).



The permanent *Mg*-hardness is usually transformed in permanent *Ca*-hardness (Eq. 10) as



For the complete Mg(OH)₂ forming reaction (as stable precipitate) (Eqs. 7-8), a high concentration of hydroxyl ions (OH⁻) must be present. This requires frequently a pH of 10.8 which is practically achieved by adding an excess of 35 mg/L lime (as CaO). The excess of added lime can be removed by carbonation with CO₂ (Eq. 5) or desulfurization (Eq. 6). In addition, some calcium ions are not precipitated or settled out in the primary treatment, and Mg(OH)₂ is soluble to about 9 mg/L which corresponds to 15 mg/L hardness as CaCO₃. With the additional CaCO₃ in solution and allowing incomplete precipitation, the final hardness can be over 50 mg/L (as CaCO₃).

Because pH must be above 9.5, recarbonation must be used to generate a product in an acceptable pH range. The most important reason for this pH reduction (till no more than 8.6) is to prevent downstream precipitation of CaCO₃ (at this pH value, CaCO₃ solubility-*S*_{CaCO3} is higher than that of its solubility product-*P*_{CaCO3}) (Zaharia, 2014). Many ions

can be precipitated by modifying the water pH, but the interaction of constituents is also important.

The required coagulant dose (i.e. critical coagulant concentration) is verified in practice by the calculation of ' $2p - m$ ' for lime dose, or ' p/m ' and ' m ' for ferrous sulfate dose, where ' m ' is the acidity of coagulated water (as HCO_3^- equivalent), and ' p ' is the alkalinity of coagulated water (as CaCO_3 equivalent).

Because of high flow rates associated with industrial water supplies, there are economic constraints on the capital and operating costs which can be incurred. These constraints limit solids removal and separation methods to gravity sedimentation and thickening, in most cases. In some cases, filtration is necessary because of residual, unsettled precipitate in the industrial water. Operating cost is considerably higher because of the required amount of chemicals addition and the increased sludge-disposal problem.

Finally, concentration and separation of primary sludge (a watery mixture of solids), or conditioning of final sludge produced from this industrial water treatment plant is sometimes required prior to the final disposal. Therefore, a gravity sludge thickening basin (multi-compartments), or, in certain cases, a gravity belt thickener (requiring polymer for sludge conditioning) is needed for primary sludge concentration and separation. The installations and types of equipment used in the primary industrial water treatment station are as follows:

- the dosing installation of lime (from 3 bins with powder lime) and ferrous sulfate (solid form, from specific deposit) (Fig. 2), equipped with specific dosing units and pumps for prepared working solutions;
- 1 primary radial settling tank ($D=20$ m, $H=5$ m, $v_s=0.3$ m/min, and around $t_s=1.5-2$ hs) (Fig. 1);
- 6 pumps for coagulated water (*Sigma* type);
- 6 mechanical filters ($D=3.4$ m, $H_t=5.5$ m, $V_t=45.3$ m³) (Fig. 1) for preliminary step;
- 2 basins with coagulated water (300 m³);
- 1 installation of compressed air (2 compression pumps of *EC10* type);
- 1 gravity (4-compartments) thickening basin (or a gravity belt thickener, only if this option is selected,

requiring polymer for sludge conditioning/concentration).

A few analyzed values of some quality indicators of coagulated water permanently controlled after the primary treatment station are summarized in Table 1, as average or mean value for 2018. Each analysis was performed in triplicate, in each month at least 10 times per week, especially in summer season (when operating at CET 1 thermal power station was activated) but also in cold season (when was worked the CET 2 thermal power station), and the standard deviation was in acceptable limit of $\pm 10\%$, in range of (-6.34 – 5.32) %.

The performance of primary industrial water treatment station is very good due to more than 90% permanent removal of suspended solids in colloidal ranges (e.g., admissible limits of turbidity under 0.5-1 FTU, with reduction or treatment degree greater than 85-90%, respecting the norms imposed in the best available techniques (BAT) for water and wastewater treatment), organics expressed as COD (removal higher than 80.00 - 87.50%) and certain analyzed dissolved substances (i.e. different cations and anions, conductivity, fixed residues, hardness etc.) as shown in Table 1. Unfortunately, the content of dissolved salts and metal ionic species is still high for use as process water in the energy sector and requires reduction in the further industrial water softening station (i.e. total hardness reduction till zero value; total iron concentration lower than 0.1 mg/l and pH of 8.5-9.5).

Majority values of analyzed quality indicators for coagulated water are in agreement with the imposed limits by the local environmental regulation authority (as shown in Table 1), but, in energy sector, the industrial process water used in the principal and secondary thermal circuits must take into account the ISCIR norms (www.iscir.ro) which impose complete elimination of a few ionic species, especially of the cations responsible for the total hardness (e.g., Ca^{2+} and Mg^{2+} cations). Therefore, in the further industrial water treatment station will be eliminated the total content of cations, especially in the form of calcium and magnesium ionic species (Ca^{2+} and Mg^{2+}) by using specific ionic exchange processes.



(a) View with lime tins, mechanical filters and primary radial settling tank



(b) FeSO_4 solution pumping units and dosing installations

Fig. 2. Views with a few installations and units used in primary industrial water treatment station

Table 1. Characteristics of analyzed industrial water in the primary treatment station (after the coagulation-sedimentation step) (inlet, outlet and maximum admissible limits)

Indicator	Measured units	Inlet (In)	Outlet (Out)	M.A.C.*	Indicator	Measure d units	Inlet (In)	Outlet (Out)	M.A.C.*
pH	-	8.5-9.5	8	7.0-9.5	COD	mg O ₂ /L	8-10	1-2	2
TSS (or turbidity)***	mg/L (FTU)	18-22 (17-15)	1-2 (0.5-1)	5 (0.02)	Fixed residues	mg/L	880-900	260-285	300
Total iron	mg/L	5	0.084	1.0	Conductivity	□S/cm	426	500	300
Alkalinity (m) (as CaCO ₃)**	mg/L mmol/L	185 3.7	145 2.9	150 3.0	Total hardness (as CaCO ₃)	mg/L mmol/L	300 3	8.68 (°G)	min. 5°G
Ca ²⁺	mmol/L	2.5	1.0	5.0	HCO ₃ ⁻	mmol/L	5.80	3.40	3.5
Mg ²⁺	mmol/L	0.5	0.54	2.0	Cl ⁻	mmol/L	1.0	0.985	7.0
Na ⁺	mmol/L	4.5	4.2	4.35	SO ₄ ²⁻	mmol/L	2.7	0.575	2.6
Σ(cations)	mmol/L	7.5	5.74	11.35	Σ (anions)	mmol/L	7.5	4.96	13.1

* M.A.C.- maximum admissible concentration for treated industrial water after primary treatment station; ** The relative alkalinity (p/m) was around the value of 0 / 2.9; *** the turbidity and other cations and anions concentrations will be minimized or even completely eliminated in the further softening step.

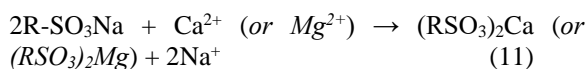
3.1.2. Industrial water softening processes and specific units

The industrial water softening station has an important role caused by requirements imposed for total hardness reduction and control of coagulated water coming from the primary treatment station (zero hardness, that means $\Sigma(\text{Ca}^{2+}+\text{Mg}^{2+})=0$), and sometimes complete demineralization ($\Sigma(\text{cations}+\text{anions})=0$).

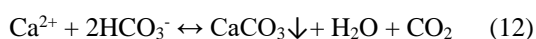
The major anions associated with dications as Ca²⁺, Mg²⁺, Si²⁺, Fe²⁺ are HCO₃⁻, SO₄²⁻, SiO₃²⁻, Cl⁻, NO₃⁻, and they are transformed in adherent precipitated particles (t ≥ 80°C) in the technological process of thermal energy generation (heating). Other fraction of anions is transformed in precipitated solids in the preliminary and primary water treatment stations, and the rest is present in coagulated water and will be completely eliminated by demineralization in the industrial water softening station, if is required.

Therefore, the coagulated industrial water is introduced in five Na-cationic-exchange units (Na-cationic filters) with ion-exchange materials of Vionit CS3 type (high acid exchanger) characterized as solid mass (granules of 0.3–1.2 mm), insoluble in water, with macroporous structure and low affinity towards hydrogen ions (H⁺); increasing cationic affinity order as H⁺ < Na⁺ < K⁺ < Mg²⁺ < Ca²⁺ < Al³⁺ < Fe³⁺.

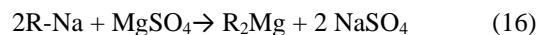
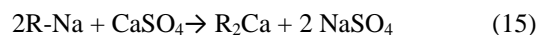
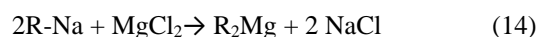
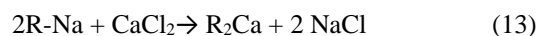
The general cationic exchange reaction corresponds to Eq. (11).



Regeneration of ion-exchange material is performed with salt solution of 7-10% NaCl. The calcium and magnesium ions presented in coagulated water, which is further used as an industrial process water in the thermal power station, can lead to boiler scale formation (on surface of heat exchangers) resulting from the decomposition of bicarbonate in steam line (e.g., CaCO₃) at high temperature, according to Eq. (12).



Therefore, all calcium and magnesium ionic species must be eliminated by ion exchange processes in the Na-cationic exchange filters before further used as industrial water in the thermal circuits of the thermal power plant based on characteristic chemical reactions as



The Na-cationic exchange filters are functioning in two steps (in series) assuring in this way the required industrial water quality according with imposed ISCIR norms (www.iscir.ro) (a two steps cycle consisting of cation exchanges followed by regeneration of exhausted exchanger material).

The basic installations and specific units used consists of:

- 5 Na-cationic exchange units/filters (D= 2.8 m, H_t= 5.1 m) (Fig. 3);
- 2 Basins with salt solution (V= 100 m³) constructed with concrete plated with anti-acid bricks;
- 4 Steel pumps for salt solution (Q=40 m³/h, 25 mCA) of DN 80-50-200 type.

The industrial water softening station achieves 100%-removal of total hardness during the entire working period of time of a year. Consequently, for the whole industrial water treatment plant, the treatment performance (i.e. pretreatment with lime followed by mechanical filtration→coagulation-sedimentation→softening, and sometimes disinfection by chlorination) is very good, being higher than 85-90% in terms of total suspended solids (TSS), turbidity, organics (expressed by COD), fixed residues, total iron content and 100% in terms of total hardness, other cations and even anions and no slime growth on cooling system, pipes and other mechanical systems.



Fig. 3. View with ion-exchange filters

Engineering responsibility for industrial water treatment must have in view performing of required water treatment degree (> 75÷85 % till 100%), correct system design and treatment operation (complete or high efficiency in each industrial water treatment station for all required pollutants removal), industrial water quality standards (both qualitative and quantitative aspects; e.g., consistent production of industrial water with low COD (<2 mg O₂/L), dissolved oxygen (around 0.02 mg O₂/L), alkalinity (m) (0.03 mg/L), total iron content (< 0.02 mg/L), conductivity (<0.3 mS/cm) and suspended solids concentrations (less than 8 mg/L regardless of influent concentrations, and pH of 8.5-9.0) and also concentration, conditioning and disposal/valorization facilities of its produced sludge (primary and desulfurization sludges), and also production wastes as slag and bottom/fly ashes).

3.3. Primary and desulfurization sludge: main characteristics, separation and valorisation possibilities

3.3.1. Primary sludge characteristics

The solids that settle to the bottom of the primary settling tank (PST) is scraped to a sump and removed by a pump. This watery mixture of solids is named primary sludge and removes between 85-90% of suspended solids, 90-95 % of settleable solids and 25-40% organics. For increasing sludge thickening and valorisation possibilities as raw material source in manufacturing of added value product (e.g. iron-based

coagulant, iron-based catalyst and adsorbent material), or as conditioning/auxiliary agents (in new composites), the primary sludge must be characterized mainly by a few principal physical-chemical quality indicators, recommended by the environmental norms and homologation standards, or requirements of different industrial products. Preliminary analysis and some analysed physical-chemical quality indicators were presented in Tables 2 and 3. Each analysis was performed in triplicate, and the standard deviation value was in acceptable limit of ± 10%, exactly in the range of (-2.86 – 3.85) %.

The prelevated sludge samples were analyzed in period of 2017-2018, especially in the cold season, during 6 months (November-April) when was operated the CET 2 thermal power station, the values presented in tables must be considered as the average/mean value of all analysed samples in this period of time. These preliminary characteristics are indicated no possibility to energetically valorize these preliminary sludges for useful thermal energy extraction due to their very low organic content, being predominantly inorganic in nature.

Therefore, some mineral constituents of this primary sludge can be valorized individually or in mixture for synthesis of new added-value products, e.g., new coagulants, or auxiliary/conditioning agents for composite products with metals in their basic matrix which can be used also as catalyst in advanced oxidation treatment of different industrial effluents.

This primary sludge has a common high water content (72.33%), very low organic content (1.25 % COD in dried substance), relative normal content of sulphates (207.5 mg/kg of dried substance) and also very low content of extractable substances in organic solvents (< 5 mg/kg) and total hydrocarbons (<5 mg/kg).

As it was mentioned above its chemical composition is predominantly inorganic with a lot of metal species (as precipitated/co-precipitated hydroxides, carbonates, sulphates, other chloride-based complexes, or oxides-hydroxides-carbonates agglomerates) in its primary sludge matrix, the dominant metals being iron (total iron content of 2,152 mg/kg of dried substance) and calcium (239.081 mg/kg of dried substance). Low toxicity can be also noted due to arsenic (1.72 mg/kg of dried substance) and tin (< 5 mg/kg of dried substance), but these values are still not critical for obligatory intervention and are considered as in approved alert level.

Table 2. Preliminary analysis of primary sludge produced

Characteristics	Results / Mean value	Analysis standard
Aspect	Solid as soft paste, yellow-brown color	Visual
Reactivity	No reactivity in water, or alkalis (1N NaOH); very strong reactivity in acid medium (1N HCl) with effervescence	Internal methodology
Behavior in contact with an ignition source	It is not burning in contact with an ignition source	Internal methodology
pH (at 25° C)	9.16	ISO 10390: 2005
Caloric power, [kcal/kg]	Not burning in the calorimetric bomb	ISO 1928: 2009

Table 3. The mean values of some physical-chemical quality indicators of primary sludge

<i>Indicator</i>	<i>Measurement units</i>	<i>Mean value</i>	<i>Analysis standard used</i>
Water content	%	72.33	SR EN 12880: 2007
Dried residue	%	26.67	SR EN 14346: 2007
Total organic carbon (TOC)	% of dried substance	1.25	SR ISO 14235
Extractible substances in organic solvents	mg/kg	<5.0	IR spectrometry
Total hydrocarbons content (TPH)	mg/kg of dried substance	<5.0	IR spectrometry
Sulfates from aqueous extract (1:5)	mg/kg of dried substance	207.4	SR ISO 11048/1999
Cadmium (Cd)	mg/kg of dried substance	<0.03	SR ISO 11047/1999
Chrome (VI)	mg/kg of dried substance	<0.005	SR ISO 11083/1998
Copper (Cu)	mg/kg of dried substance	<0.2	SR ISO 11047/1999
Nickel (Ni)	mg/kg of dried substance	<0.2	SR ISO 11047/1999
Lead (Pb)	mg/kg of dried substance	<0.3	SR ISO 11047/1999
Arsenic (As)	mg/kg of dried substance	1.72	AAS –hydride technique
Selenium (Se)	mg/kg of dried substance	<0.015	AAS-hydride technique
Mercury (Hg)	mg/kg of dried substance	<<0.003	AAS-hydride technique
Antimony (Sb)	mg/kg of dried substance	<0.5	EPA 7000B/2007
Tin (Sn)	mg/kg of dried substance	<5.0	EPA 7000B/2007
Calcium (Ca)	mg/kg of dried substance	239.081	EPA 7000B/2007
Total Iron (Fe)	mg/kg of dried substance	2152	EPA 7000B/2007

Moreover, this primary sludge was accumulated all three toxic heavy metals (Cd, Pb, Hg) but their contents are very low being considered as ‘in traces’ (<0.003 mg/kg of dried substance) for Cd and Hg, and more than 100 times higher but not critical (in approved admissible limits) for Pb content (<0.5 mg/kg of dried substance).

Finally, the characteristics of this primary sludge are corresponding to those of inorganic wastes grouped in 19 09 02 coded categories (sludges from water clarifying) that can be easily stabilized by inertness in cement concrete matrix (or other composite matrices) and vitrifying.

3.3.2. Characteristics of the desulfurization sludge

For degasifying, or control and reduction of polluting species from gaseous combustion flux it is used commonly chemical degasifying with lime for the elimination of CO₂ and SO₂ by carbonation and desulfurization processes when are formed precipitates/co-precipitates of calcium carbonate and

calcium sulphate or sulphite. The solubility of these precipitates is strongly influenced by pH, stable precipitates being formed in strong alkaline pH range (pH>10.6) (in excess lime solution). A preliminary analysis and some physical-chemical quality indicators were presented in Tables 4 and 5.

The preliminary analysis confirms the high stability of desulfurization sludge caused of its very high pH range (pH>10.6), and utilization of significant amount of ‘in excess’ lime (due to very high pH value of 12.69). It must be also mentioned that each analysis was performed in triplicate, and the standard deviation value was in acceptable limit of ± 10% (in range of - 3.32 – 4.92) %.

The prelevated desulfurization sludge samples were analysed in period of 2017-2018, in the cold season (November-April, 6 months) when was operated the CET 2 thermal power station, all values presented in tables must be considered as the average/mean value of all analysed samples in this period of time.

Table 4. Preliminary analysis of desulfurization sludge

<i>Characteristics</i>	<i>Results / Value</i>	<i>Analysis standard</i>
Aspect	Solid as powder, grey-black	Visual
pH (at 25° C)	12.69	ISO 10390: 2005

Table 5. The mean values of some physical-chemical quality indicators of desulfurization sludge

<i>Indicator</i>	<i>Measurement units</i>	<i>Mean values</i>	<i>Analysis standard</i>
Water content	%	72.33	SR EN 12880: 2002
Dried residue	%	27.67	SR EN 14346: 2002
Calcium	%	18.19	EPA 7000B/2007
Sulphates	%	3.68	STAS 11048/1999
Sulphites	mg/kg	50.50	Spectroquant Merck

The physical-chemical analysis results indicate a high water content (72.33%) which is a relative common content in a separated sludge, and high calcium content (27.67%) in the dried residue predominantly as sulphite (50.50%) but also low sulphate (3.68%) forms, being evidently its normal production in a desulfurization step, meaning SO₂ elimination by absorption in alkaline solution such as only lime solution, or mixed soda (Na₂CO₃)/lime solution system. This desulfurization sludge is stable in very alkaline conditions and can be valorised in neutralisation treatment processes of very acidic media for minimization of corrosion problems and also to control and reduce the acidification in different aqueous environments and/or soils.

3.4. Disposal and valorization possibilities of primary and desulfurization sludge (individually or in mixture with other solid production wastes generated in the thermal power plant)

The primary sludge from industrial water treatment plant must be separated and disposed of, usually by thickening using two ways chosen based on company economic situations in a certain period of times, or strict imposed environmental managerial initiatives, each one with its merits, as:

(i) A first open *gravity thickening basin* with four compartments receiving the incoming sludge in each compartment (fresh or diluted ones), the sludge having only a certain odor and settleability problem in summer (evaporation and gravity separation being the predominant active forces). Usually, after one or two

months, the concentrated sludge is transferred with the help of a vacuum system onto the disposal platform (CET II Holboca, Iasi) of the production wastes (ashes, slag, neutralization wastes, among others), in a specially designed location place. The resulted sludge quantity is of 15 – 20 t/month and has the pH of 9-10.

(ii) A secondary closed *gravity belt thickener* (Fig. 4) in which polymer (polyelectrolyte) is required, recommended with centrifuge, having a certain problem with chemicals and electricity, when centrifuging and belt is working. Mechanical dehydration operates when the mixture of polymer and sludge is spread across a horizontal porous belt allowing water to drain down by gravity and solid concentrated plates (blocks) to be formed and transferred with trucks to company depositing/disposal platform of production wastes (CET II Holboca, Iasi). Polymer feed is important; the amount of polymer as well as agitation regime must be determined by experimental study for each specific sludge. The recommended polymer concentration is in the range of 50-150 mg of polymer/L of sludge in two agitation steps (a rapid one of 250-300 rpm for 3-10 minutes, and a second slow one of 30-50 rpm for 15-30 minutes).

Also the belt speed must be set properly, a belt slowly operated is recomandable. In this context, the gravity belt thickener operates as follows: the sludge is pumped into the conditioning thickening unit with centrifuge by a delivery pump (a centrifugal sludge trap, in fact a rotating drum, consisting of a helical rotor with an independent rotation movement related to that of rotating drum).



(a) Ready-to-use polymer injection system



(b) Installation for polymer preparation



(c) Conveyor belt for sludge dehydration



(d) Collecting unit of concentrated solid plates

Fig. 4. Views with gravity sludge belt thickener (polymer required, and centrifuge recommended)

The ready-to-use polymer is continuously introduced in the conditioning unit and added to sludge proportional to the solid amount. While the sludge is gently conveyed on a slowly operating conveyor belt, the filtrate (separated water) is collected and used for polymer preparation. The conditioning tank and ready-to-use polymer preparation system is controlled by a process computer and visualized on a control panel (Fig. 4b).

The dehydrated sludge is discharged directly into a container. After filling, the container is transported with a truck and cleared to the company disposal platform of slag and ash (CET II Holboca, Iasi). The resulted sludge quantity is of 16 – 22 t/month and has the pH of 7.5-9. This second sludge belt thickener offers benefits as (i) reduced size of dehydrated sludge; (ii) low washing water demand and relative low energy demand; (iii) odor-free station; (iv) wear is reduced to a minimum and noise eliminated due to the slow speed of the conveyor belt, and (v) high operational reliability.

For the company actual economic situation it is enough the gravity thickening basin used. Other solid wastes produced in the thermal power station (slag, bottom/fly ash, neutralization wastes, having low price, low polluting effects, continuous processing possibilities, high hydrophilia) are usually stored onto the company disposal platform (CET II Holboca, Iasi) and properly valorised, when is possible. A few cert possibilities of sludge valorisation, individually and, in mixture with other production wastes, is

summarized in Table 6.

Conclusions

The industrial process water of Veolia Energy Iasi Company requires continuous and efficient treatment in its mechanical-physical-chemical treatment plant, which is presented in detail, for the first time, in this work, this treatment plant being adapted to operate in different extreme economic situations and also to be in agreement with all consumers' requirements.

Therefore, three industrial water treatment stations, i.e. the preliminary (degasifying by absorption in lime solution), primary (coagulation-sedimentation) and softening (ion exchange process) treatment stations, were described referring to its unitary processes/operations, mechanisms, installations, performance achieved, and also the quality characterization of its treated industrial process water and certain types of produced sediment and sludge. A few valorization directions of solid sludges and production wastes were recommended in association with the already performed scientific researches and reported data sources. Moreover, Veolia Energie Iasi Company is still considering the industrial water quality as a key factor in ensuring of good and efficient operating conditions of its thermal power station in association with the good quality products/byproducts offered on the free market of products/services.

Table 6. Certain valorisation directions of individual and ,in mixture' sludge with certain production wastes of Veolia Energie Iasi Company (slag, ashes and neutralization by-products)

<i>Valorisation direction</i>	<i>Possible application</i>	<i>Reference</i>
Added-value product preparation/ synthesis (e.g., utilisation as -binding material, -auxiliary material, -conditioning agent, -raw matter, etc.)	- manufacturing of ceramic composites (bricks, Ceramica Iasi Co., RO), or other composite types	Ponkarthikeyan et al., 2016; Zaharia, 2018
	- preparation of construction materials, after stabilisation by inertness in cement concrete matrix, or vitrifying, - production of cement/consolidated concrete used in eco-industrial parks, - synthesis of polypropylene fiber/high calcium fly ash geopolymers, geotextiles, or derived sawdust as specific mixture of sawdust-ash	Chindaprasirt and Rattanasak, 2017; Guo et al., 2017; Ciocan et al., 2017; Harja et al., 2009; Kong et al., 2017; Lepadatu et al., 2018; Niculita et al., 2017; Rattanasak, 2017; Serbanoiu et al., 2017; Sua-Ian and Makul, 2017
	- preparation of magnetic zeolitic materials obtained from coal fly ash in mixture with magnetic zeolites	Shoumkova and Stoyanova, 2017
	- new iron (metal)-based catalysts in effluent treatments, - new coagulants in water/wastewater treatment	Zhang et al., 2012; Wang et al., 2017
Neutralization / soil remediation	- new adsorbent material for persistent organic and heavy metal species removal, discoloration purposes, different hazardous organics removals from industrial effluents	Harja et al., 2010, 2011; Willett et al., 2019; Zaharia, 2015, 2018; Zaharia and Suteu, 2013; Zhao et al., 2016
	- aggressive reduction of industrial effluents, or aqueous environments due to sulfates or acidic species; - reduction of soil acidity (use as soil conditioning agent) or other soil remediate actions and improvements in agricultural cropping	Abdelhadi et al., 2018; Cocarta et al., 2017; Masu et al., 2016; Singh et al., 2016; Yuyou et al., 2016; Yu et al., 2017

The company is continuously interested in maintenance of high performances of all industrial water treatment stations and also its efficiency improvement and/or technical modernization.

This addresses especially the automatic control of involved production processes and operations by investments in new advanced high-tech systems, and also initiating of preventive, treatment and valorization actions of its produced sludge/waste for possible homologation of new added-value products, or useful substance recovery for different industrial purposes.

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