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Treatment of Wastewater from Wet Scrubbers in Secondary Lead Smelters for Recycling and Lead Recovery

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***Abstract*—**The present study shows a method to recover lead metal from wastewater of wet scrubber in secondary lead smelter. The wastewater is loaded with 42,000 ppm of insoluble lead compounds (TSP) submicron in diameter. The technical background benefits the use of cationic polyfloc solution to flocculate these colloidal solids before press filtration. The polymer solution is injected in the wastewater stream in a countercurrent flow design. The study demonstrates the effect of polymer dose, temperature, pH, flow velocity of the wastewater and different filtration media on the filtration extent. Results indicated that filtration rate (f_r), quality of purified water, purifying efficiency (f_e) and floc diameter decrease regularly with increase in mass flow rate and velocity up to turbulence of 0.5 m.sec^{-1}. Laminar flow is in favor of flocculation. Polyfloc concentration of 0.75 – 1.25 g/m^3 wastewater is convenient. Increasing temperature of the wastewater and pneumatic pressure of filtration enhances f_r. High pH value deforms floc formation and assists degradation of the filtration fabric. The overall efficiency of the method amounts to 93.2 %. Lead metal was recovered from the filtrate cake using carbon as a reducing agent at 900°C.

***Keywords*—**Wastewater, wet scrubbers, filtration, secondary lead.

I. INTRODUCTION

PURIFICATION of wastewater have drawn increasing research awareness applying different treatment techniques such as physical, chemical, anaerobic/aerobic, drum and disc filtration, membrane filtration, advanced oxidation systems, and equalization tanks. Conventional technology of wastewater treatment includes removal of grease and oil, minerals, pesticide and de-colorization, sludge dewatering, nitrification and de-nitrification, facilitative lagoon. Rose et al. [1] showed the methods include flocculation, sedimentation [2], flotation froth flotation and fuzzy filters. Sedimentation is a primary stage in modern wastewater treatment plants reducing the content of suspended solids as well as the pollutant embedded in the suspended solids [3]. Sansalone et al. [4] reported that significant decrease of turbulence, particle mass (measured as total suspended solids, TSS) and volume concentration generated by alum and ferric chloride consistently occurred at a ξ potential in the range of −15 to about −10 mV. Alum addition produced a charge reversal at dosing above 60 mg/L (18×10^{-5} M) while ferric chloride did not reverse charge. With respect to turbulence and TSS decrease, alum outperformed ferric chloride, without the need for pH control. Amuda and Amoo [5] showed that the combined use of coagulant and polyelectrolyte decreased the sludge volume with 60%, compared to the use of the coagulant alone. They concluded that coagulation / flocculation might be a useful pre-treatment in wastewater processing. Ebeling et al. [6] claimed that orthophosphate removal efficiency with alum and ferric chloride was 89 and 93%, respectively, at a dosage of 90 mg/l. The use of 60 mg/l dosage for both alum and ferric chloride caused optimum turbulence removal. Both alum and ferric chloride demonstrated excellent removal of suspended solids from initial TSS values of approximately 100–10 mg/l at a dosage of 90 mg/l. Flocculation and mixing speed played only a minor role in the removal efficiencies for both orthophosphates and suspended solids. Both coagulation–flocculation aids also exhibited excellent settling characteristics, with the majority of the floc quickly settling out in the first 5min. El Samrani et al. [7], showed the nature of coagulant species that are dependent with Fe concentration. Mainly iron dimers linked with one phosphate anion detected the optimum turbulence removal. At higher dosages, polymers of hydrolyzed Fe appeared even though PO_4 still participates in the formation of coagulant species. Analyses revealed that minute amounts of sulfur, silicon, aluminum, and calcium associated with the coagulant species. Goren et al. [8] showed that 10- and 2-kDa membranes operated without pretreatment provided 45% TOC retention. With proper pre-treatment, the smaller membrane pore size the more significant the contribution. James et al [9], evaluated six polymers to estimate the optimum polymer dosage for flocculation of aquaculture micro-screen effluent and overall solids removal efficiency. Results showed TSS removal was close to 99% via settling, with final TSS values ranging from as low as 10–17 mg/L. Dosage requirements were fairly uniform, requiring between 15 and 20 mg/L of polymer. Using these dosages, estimated costs range from $4.38 to $13.08 per metric ton of feed. Hirosue et al. [10] found that the most important factor in coagulating red mud is maintaining the pH of solutions in suspensions within the range of 7 to 8 regardless of red mud concentration. This criterion is because the zeta potential of red mud in that pH range was less than approximately 13 mV. Shon et al. [11] studied the effect of partial flocculation and adsorption as pretreatment to ultra filtration. Their results were in line with that claimed by Goren et al. [12]. The coke is used

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to melt and reduce the lead. Limestone reacts with impurities and floats to the top. This process also keeps the lead from oxidizing. The molten lead flows from the blast furnace into holding pots. Lead may be mixed with alloys, including antimony, tin, arsenic, copper and nickel. It is then cast into ingots [13].

The objectives of this paper are to study the factors affecting purifying and of wastewater purging from a wet scrubber in lead smelter and recycling the purified water in the scrubbing facility. The impact of the applied technology on the process economics and quality of the treated water is given.

II. EXPERIMENTAL

A. Materials

1. Lead smelter and refining Co. of Egypt (10,000 t lead/y) provided the facility of wastewater (10m^3/h) sample from a wet scrubber furnished at the plant.
2. Thick cotton, Nylon and silkscreen cloths Nr 1000 and 1200 samples (Switzerland) having different pore size, were investigated for filtration in a lab filter press (0.04 m^2 area).
3. Chemicals used for flocculation, coagulation and chemical analysis were technical pure grade. Polyfloc of Cyanamid, France, [14] is the material for coagulation / flocculation purposes. Polymer solution containing 0.75 mg up to 1.0 mg /L was prepared. A drop of chloroform was added before storing in polyethylene tank.
4. Doubly distilled water is used for chemical analysis, whereas tap water was used for other purposes.

B. Wet Scrubber

Details of the wet scrubber design and operation conditions were published elsewhere, Rabah [15].

C. Description of the Test Facility

Fig. 1 shows a schematic diagram of the testing facility. The polyfloc material was dissolved in water to a concentration of 0.1 g/L. Storing of the solution was no more than 48 hours before use. The solution storage tank was connected to a pump-driven syringe (Nr. 14) penetrating the wall of a pipe connecting the wastewater tank to a settling tank. The volume flow rate of both the wastewater and the polyfloc solution was adjusted with the help of a precise flow meter connected with a pneumatic valve. Purified water after filtration was analyzed to determine its quality in terms of total solid content, the values of filtration rate (f_r) and purifying efficiency (f_e). Sedimentation rate was determined gravimetrically in a side-bench facility as given by Rabah [15].

D. Methods of Measurements

1. Volume flow rate of the wastewater stream was carried with the help of a digital precise flow meter type CZ-33117-30, Cole-Parmer, USA.
2. Determination of lead was carried out gravimetrically as lead chromate.
3. Determination of the extent of purity of the filtrate was carried out in terms of total solids content (TSP). Total solids of the raw wastewater was taken as blank (100) whereas that of distilled water = zero. The extent of purity percentage for the purified water = (100–TSP $_{\text{sample}}$) x 100.
4. Determination of sedimentation rate, filtration rate (f_r) and purifying efficiency (f_e) were conducted gravimetrically applying standard methods given in the literature, Rabah [15].
5. Particle size measurement was determined using a SediGraph-5100 particle analyzer, Micrometrics, USA and X-ray diffraction equipment model PW/1710 with Ni-filter, Cu radiation (θ = 1.542) at 40kV, 30 mA and scanning speed 0.02° /s.

III. RESULTS

Table I shows the composition of the dirty wastewater coming out from the wet scrubber.

TABLE I
THE COMPOSITION OF THE LOADED WASTEWATER COMING OUT FROM THE WET SCRUBBER

Sample	T°C	TSP, ppm	Insol .solids mg/L	pH value	Particle size distribution, wt %		
					<1 µ	<0.1	<0.05
1	55	42500	42.25	4.2	100	40	25
2	55	42480	41.80	4.8	100	30	40
mean	55	42490	42.02	4.5	100	35	32.5

It can be seen that the total insoluble solid particles (TSP) amounts to 42.02 mg/L. Particle size distribution shows that all particles are submicron in diameter.

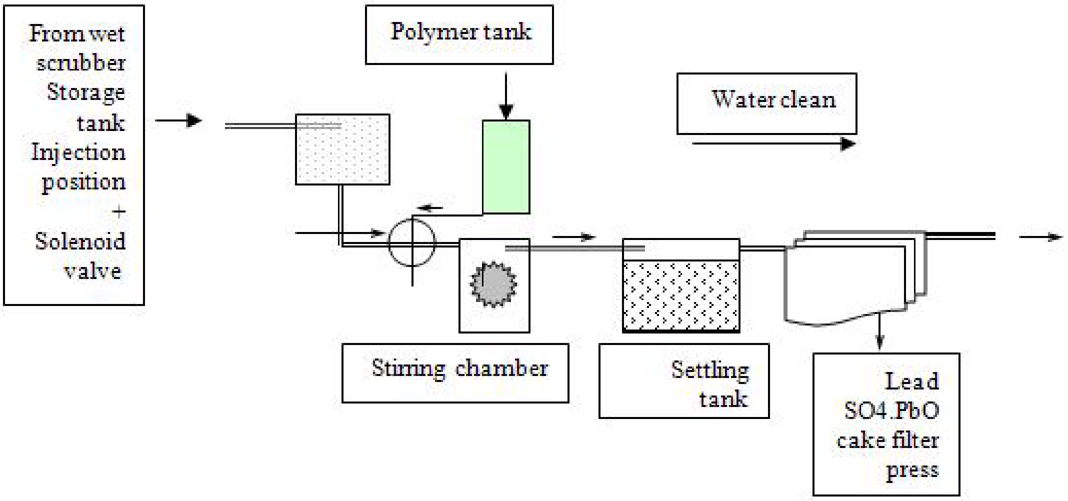

Fig. 1 A schematic diagram of the testing facility

Fig. 2 shows the effect of filtration pressure, in KPa, on the filtration rate and the extent of purity of the treated water at ambient conditions (T=32°C without flocculants). It is seen that at 100 KPa, the filtration rate was 50 L/min/m^2 (≈5 m^3/h). Filtration rate increases gradually up to 160 L/min/m^2 with increasing the filtration pressure to 200 KPa. The industrially recommended extent of filtration rate of 100 L/min/m^2 (≈10 m^3/h) has been attained at 170 KPa.

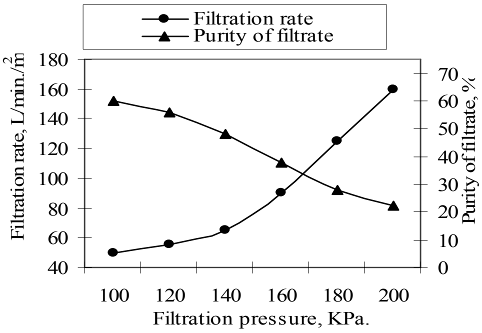

Fig. 2 Effect of filtration pressure on the extent of filtration using silkscreen 1000 recommended filtration rate

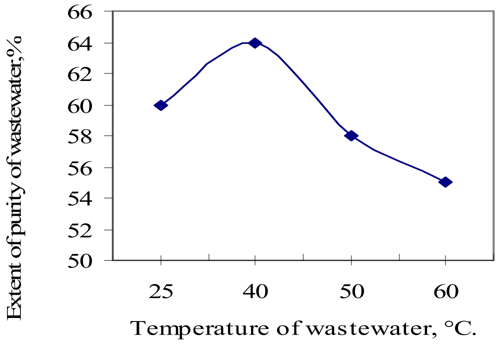

Fig. 3 Effect of temperature of wastewater on the extent of purity of the reclaimed water using silkscreen 1000 as a filter

However, increasing the filtration pressure is against the quality of the purified water. Fig. 3 shows the effect of temperature on the extent of filtration rate using silkscreen 1000 as a filter. It can be seen that increasing the wastewater temperature up to 40°C improves the quality of the purified water. The quality of the produced water decreases with further increase in temperature. Fig. 4 shows the effect of filtration pressure (*f*p) on the filtration rate (*f*r) using different filtering media. It can be seen that *f*r increases gradually with increasing the *f*p. It is also noted that *f*r increases in the order silkscreen, cotton and nylon filter.

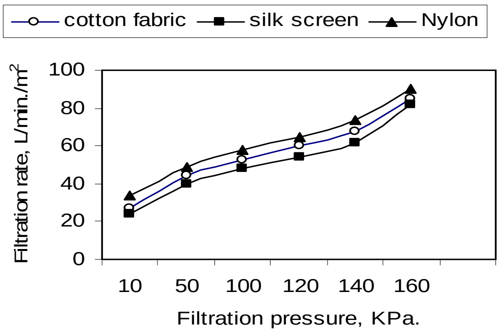

Fig. 4 Effect of filtration pressure on the filtration rate using Cotton fabric, silkscreen and Nylon filters (T= 25°C, P=10KPa.)

Fig. 5 shows the time required to undertake floc formation as affected by the flocculent dose. Experiments were carried out at different temperatures up to 50°C, the practical temperature level of the industrial wet scrubber. It can be seen that cooling the wastewater down to nearly the ambient conditions increases the time necessary to accomplish floc formation. Increasing the flocculent dose enhances floc formation in less session.

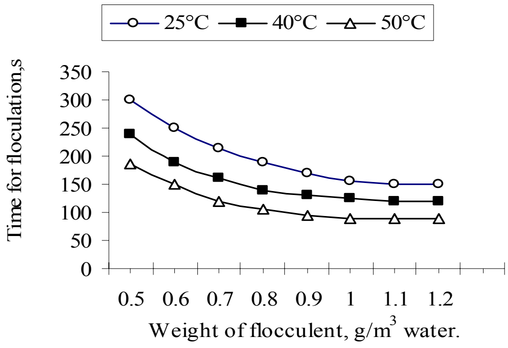

Fig. 5 Effect of weight of flocculent in wastewater on time for flocculation

Fig. 6 shows the effect of flow velocity of the wastewater stream on the mean diameter of the floc so formed. It is seen that under laminar flow condition (≤ 4 m.s^{-1}), the floc diameter is kept stable at ≥ 1mm. Increasing the flow velocity to the turbulence conditions (≥4 m.s^{-1}) deforms the floc size. Solid fine particles are freed once again. In other words, the fine particles are released.

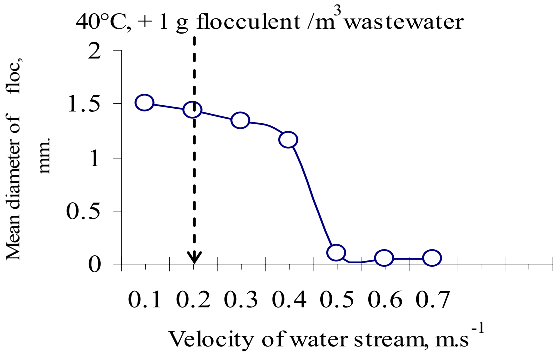

Fig. 6 Effect of velocity of the wastewater stream on the mean diameter of the formed floc

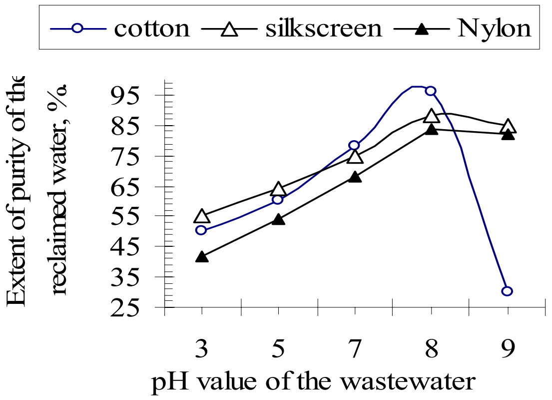

Fig. 7 Effect of pH value on the extent of purity of the reclaimed water (T= 50°C, *f*p = 100 KPa ------- industrial, acceptable values)

Fig. 7 shows the effect of pH value of the wastewater on the quality of the purified water using the three filtering media. The temperature of the raw water was 50°C and filtration was manifested at 100 KPa. Results revealed that the quality of the purified water is highly affected by the pH value. High acidity (pH<2) or alkalinity (pH>8) decrease the quality of the purified water to unacceptable value (85%). It is worthy to note that filtering cloth made of cotton fabrics is chemically more resistance to alkalinity whereas silkscreen filter is the most resistant in acid medium. Slight alkalinity helps to achieve quality water meeting the specifications, but neutral or acidic wastewater failed. Fig. 8 shows the extent of reduction of the filtered lead compounds as a function of temperature using carbon as a reducing agent.

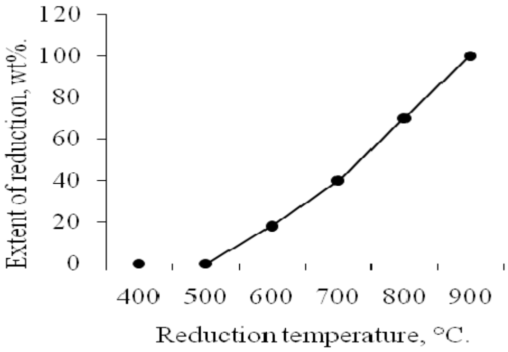

Fig. 8 Extent of reduction of lead cake using carbon as a reducing agent

Fig. 9 shows the total efficiency of the method of this work. It is seen that the filtration, lead recovery and overall efficiency extent values amount to 97, 96 and 93.2% respectively.

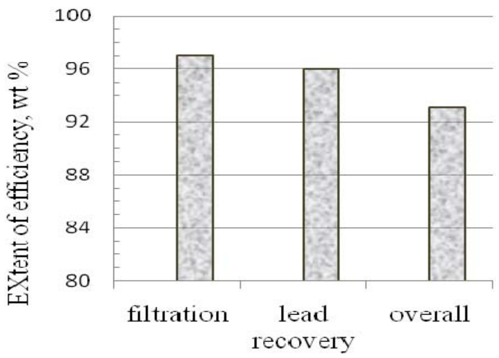

Fig. 9 The extent of efficiency of the method used

IV. DISCUSSION

Wet scrubber is equipment used for purifying hot flue gases to get rid of the fugitive emissions. Water is the conventional fluid used to collect and carry the solid particles to a discharge tank. Wet scrubber is furnished with spray towers and packed scrubbers. Normally the gas flow in the scrubber is counter to the liquid flow... The loaded gas passed through a chamber containing wetted 'packing' or sprayers. In our study, the exit wastewater coming out the scrubber is loaded with 42000-ppm insoluble solid. It becomes highly recommended to purify the wastewater to score dual goals. The separated solids contain high value lead compounds and the purified water is recyclable. Impingement of solid particles achieved successful separation of solids. According to IUPAC [2], flocculation is a process of contact and adhesion to form larger-size clusters. Flocculation is the stage where destabilized colloidal particles (or particles formed during the stage clotting) are assembled to form large aggregates easily settleable. The flocculants clarified water and impinged solid particles to enable quick and easy separation from the water.

Fig. 1 shows the sequence of the processes applied in this work. The wastewater, under investigation, coming out from the wet scrubber is loaded with 42,000 ppm (4.2%) of solid particles. It purged during the thermal recovery of secondary lead metal in short rotary furnaces from spent acid lead batteries. The particle diameter of the major part of these emissions is submicron. Chemical analysis revealed that it is lanarkite (lead sulfate-oxide ($PbSO_4.PbO$). Complying with law for environment management, secondary lead smelters install wet scrubber to capture the fumes from the flue gas. The recovery process of secondary lead involves thermal reduction of the spent battery blocks (8 tons in one charge) at ≈ 1450°C for 6 hours. Because the battery blocks contain appreciable amounts of lead oxide and lead sulfate altogether with metal lead (block frame), some of these materials escape as fumes in the flue gases. Temperature of the exit flue gas records 750-850 °C at the exit opening of the furnace and cool down to 250-300 °C at the inlet orifice of the scrubber. In the scrubber, heat transfers from hot flue gases to water mainly by conduction and partially by radiation. It becomes legitimate that the temperature of the spraying water increased. Temperature of the outlet water (T_{ow}) can be derived from the following equation:

$$T_{ow} = [M_{fg}\,(T_{ig} - T_{og})Cp_g + M_s\,(T_{is} - T_{os})Cp_s] - M_w.\,(T_{ow} - T_{iw}).Cp_w - k.f.r$$

where: T= temperature, K, M = mass flow rate, kg/h, Cp = specific heat, kJ/kg.K,
K = constant, f = fraction of energy transfer, r = radiation constant.
Subscript: f = for flow, i = for inlet, o = for outlet or exit, s = for solids, g = for gases and w = for water.

The values for K, f, and r were found to be 0.15, 0.38 and 0.09 respectively. The T_{ow} value amounts to 52°C in summer and 35°C in winter. Experiments of this work were carried out within the temperature range 25-60°C to comply with plant conditions and consider the chemical stability of the flocculent material.

Results of Fig. 3 show that increasing the filtration pressure helps the filtration process to take place at a higher rate. Pressure exerts extra forces on both solid and liquid phases to pass through the porous system of the filter media more freely. Under these conditions, ultra fine particles would escape to the filtrate. The quality of the purified water gradually decreases. Deposition and trapping of the solids in the pores (fouling) of the filter pad initiates and gradually propagates. Blocking of the pores accessible to filtration would decrease the filtration rate under normal pressure but such effect weakens as the filtration pressure increases.

In Fig. 3, the effect of the wastewater temperature indicates that filtration process becomes easier with rise in temperature of the fluid. This criterion finds support on basis of the decrease in viscosity of wastewater (0.8904 cp at 25°C and 0.5468 cp at 50°C [16]. Hot water with low viscosity would flow through the filter pore system more easily as compared to cold water.

Regarding the effect of flocculation, formation of flocks from the dispersed particles helps the filtration process. The pore diameter renders impervious to flocks with larger diameter while is still permeable to water. Fig. 5 confirms that increasing the flocculent dose caused formation of stable flocks having large size. The mean diameter of flocs agglomerated with 1g flocculent/m^3 wastewater amounts to nearly 2mm compared to 0.005mm of the porous system.

Fig. 6 demonstrates that increasing the velocity of the wastewater stream towards the turbulence flow conditions (≥ 0.5 m/s) deforms the flocs whereby fine particles regenerate. It is therefore highly recommended that laminar flow conditions of the flocculated wastewater stream are a most to safely accomplishing successful filtration.

The effect of pH value is rather of interest. Increasing the pH value of the wastewater from its original value (4) to 7-8 benefits the purity of the filtered water. This is ascribed to the chemical stability of the flocks so formed in slightly alkaline medium. With further increase of the pH value to 9 or more, a rapid and drastic decrease in the extent of water quality takes place. High alkaline water enhances chemical degradation of silkscreen and nylon fabrics examined in this work. On the other hand, hyperacidity attacks cotton fabric. Measurement of the chemical stability in neutral solution shows that it is in the order cotton, silkscreen and nylon. Whenever purification of the wastewater takes place under the controlled conditions, the quality of the produced water was in a good agreement with the technical specification. The calculated efficiency of purifying process amounts to 90.5%. Thermal recovery of the lead bearing cake (the filtrate) using carbon as a reducing agent proceeds in a multistep sequence involving reducing PbO_2 to PbO to Pb_2O_3 and finally to lead. With $PbSO_4$, it is reduced to sulfite, then sulfide then to lead metal. The overall efficiency extent of the method amounts to 93.2 weight percent.

V. PRELIMINARY PROCESS ECONOMICS

A preliminary process economics have been studied for wet scrubber using 30 m^3 water/hour. Results show that the annual running cost amounts to nearly USD 22,400 and the saved products amounts to USD 25,000 corresponding to a net gain of 11.4%. Details of this economic study are under publication elsewhere.

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VI. CONCLUSION

The output conclusion of this work is that purification of wastewater used to abate emissions of secondary lead smelter successfully achieved many advantages. The applied technology has its basic design to inject cationic polyfloc solution in the wastewater stream. Adjusting the pH value ≈ 6, temperature at <35°C and flow rate at laminar flow conditions and pressure of ≈ 150 KPa would promote high quality of the purified water. Purification process benefits the following.

- The process is economically and technically feasible.
- It saves 11.4% money.
- Abate pollution hazards of lead dissemination in the environment.
- The method is simple and the facility is rather available.

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