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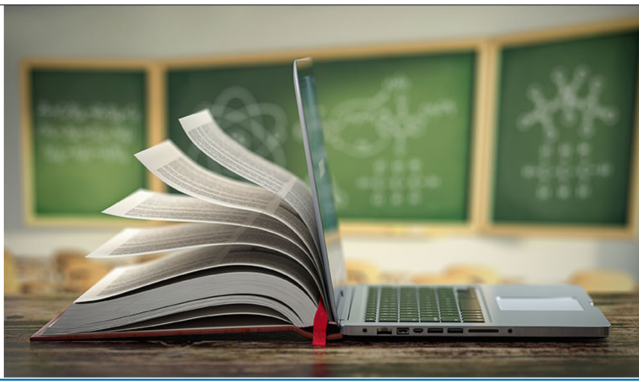

Zero Liquid Discharge (ZLD) Industrial Wastewater Treatment Systems as Sustainable Development Basic Ecological Components

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Abstract. The problems in processing the acid ferrous-containing rinsing water and spent pickling solutions are considered. The first-ever in metallurgy zero liquid discharge (ZLD) industrial wastewater treatment systems of a transformer cold rolling plant at the Verkh-Isetsky steelworks in Sverdlovsk (now — LLC VIZ Steel is a part of Novolipetsk Steel Group of Companies) is described. The experience of the VIZ Steel, particularly in relation to industrial wastewater treatment and sludge processing, is useful for designing ZLD industrial wastewater treatment systems of metallurgical, machine-building and metalworking enterprises. The recommendations for organizing the ZLD industrial wastewater treatment systems in the pickling plants with the repeated use of the treated rinsing water and processing the spent pickling solutions and the sludges are presented. For practical calculations of clarifiers the empirical formulas are offered. Process flow diagram of acid ferrous-containing rinsing water treatment is suggested. Acid ferrous-containing rinsing water treatment includes the following processes: rinsing water neutralization to pH 9–10,5 by 5 % calcium hydroxide and partial ferrous oxidation by air; addition of anionic flocculant and active gypsum priming to the neutralized rinsing water; settling of rinsing water conditioned by reagents in clarifiers; treatment of clarified water on deep bed sand filters; reclaimed water treatment.

Keywords: Zero liquid discharge (ZLD) systems; Acid ferrous-containing rinsing water treatment; Rinse pickling solution; Industrial wastewater sludge processing

1. Introduction

The creation trend of industrial plants zero liquid discharge (ZLD) systems is clearly traced in majority of advanced countries of the world during the last 15–20 years [1–4]. The reasons, causing beginning of widespread ZLD systems development, are, on the one hand — catastrophic natural water bodies pollution with industrial, domestic and agricultural wastewater [5–8] and, on the other hand — appearance of various technological equipment (multi-stage evaporating devices [9], reverse osmosis installations [10–12] etc.), which application provides acceptable economic indicators of ZLD systems. Nowadays an implementation of ZLD industrial wastewater systems is the only rational solution of the industrial water reclamation and reuse issue.

Russia has experience of ZLD systems development and exploitation The first-ever in metallurgy ZLD systems of a transformer cold rolling plant, which is still in exploitation has been put into operation at the Verkh-Isetsky steelworks in Sverdlovsk (1973) (now — LLC VIZ Steel is a part of Novolipetsk Steel Group of Companies) [13].

In the early 1980s a small group of recycling experts started talking about the idea of «Total Recycling». Zero waste concepts followed. By 1990, activists in the Philippines were already using the term zero waste. One of the first formal zero waste policies was created in 1995 when Canberra, Australia endorsed a goal of «No Waste by 2010». Since 1995, zero waste has been endorsed as a goal by governments in New Zealand; Denmark; Seattle, Washington; Del Norte County, California; San Francisco, California; Santa Cruz County, California; Edmonton, Alberta; Ottawa, Ontario; and Nova Scotia. Furthermore, a number of national and international businesses have adopted some zero waste principles [14].

2. Zero Liquid Discharge System of VIZ Steel (Novolipetsk Steel Group of Companies)

Verkh-Isetsky steelworks ZLD system was created during the solving process of industrial wastewater treatment and reuse issue. Industrial wastewater of Verkh-Isetsky steelworks can be divided into nine categories: four-high rolling mill wastewater containing palm oil or its substitutes; electric insulation coating units and decarburization annealing units wastewater, which contain fine magnesium oxide; wastewater from rolling mill carters washing; containing oils and suspensions; acid ferrous-containing rinsing water from pickling plant; spent pickiling solutions from pickling plant; spent oil emulsions; spent degreasing solutions; degreasing installation washing water; oil emulsion systems washing water. During the ZLD system development the industrial wastewaters were integrated by types of pollution in four groups:

- spent pickling solutions;
- rinsing water;
- wastewater containing oils;
- wastewater polluted by mainly mechanical impurities.

For each wastewater group the appropriate treatment facilities have been designed and constructed, placed in several buildings. After treatment water is reused in production. Liquid and solids wastewater sludges are exposed to mechanical dewatering, drying and utilization. Oil-containing waste goes for burning, and salted bleed water — for evaporation with receiving desalinated water and concentrate of salts.

The issue of rinsing water and spent pickling solution treatment and reuse is not solved at the most metallurgical plants of Russia. Contrary to the known and approbated recommendations [15, 16] rinsing water and spent pickling solution are mixed with each other and neutralized with calcium hydroxide. Then, in best case, neutralized wastewater is settled with subsequent dumping of poor quality clarified water into water body and sludge pumping to the storages. In worst case — pumping to the storages without sludge removal. As the way of chemical metal-stripping procedure by pickling in acids (usually in sulfuric and hydrochloric acid) remains the basic, consumption of acids increases by these purposes every year. So the volumes of acid ferrous-containing rinsing water and its sludge placed in storages are also increase. Because of this, the technical solutions realized during development of the Verkh-Isetsky steelworks ZLD system are relevant at present time.

3. Results and Discussion

3.1. Rinsing Water Treatment

It's important to pay attention to that low-concentrated rinsing waters (0.6–0.8 g/L of H_2SO_4, 1.8–2.5 g/L of Fe^{2+}) should be processed separately from concentrated spent pickling solutions (40–150 g/L of H_2SO_4, 80–150 g/L of Fe^{2+}) with receiving purified water which is reused and dewatering sludge which is directed to the utilization.

The main stage of acid ferrous-containing rinsing water treatment is their neutralization. With calcium hydroxide using significant solid phase quantity is formed. And it is necessary to separate it in the clarifiers. At the same time the structure of the formed flocs is of great importance: large and dense particles quickly settle and the sludge occupies smaller volume and in further easily gives to mechanical dewatering.

In most cases about measure of different factors influence on the flocs structure judge by the particles settling velocity. In case with considered acid ferrous-containing rinsing water the settling velocity depends on quantity and quality of ferrous hydroxide flocs as they settle much more slowly than other impurity (figure 1).

Sludge formed during neutralized rinsing water settling undergoes changes in time. Flocs with very small density are formed initially, then they are gradually crushing during 2–3 h. After 20–25 hours flocs begin to be integrated, further the sizes of flakes change slightly, their dispersion decreases and density increases.

Flocs sedimentation and further formed sludge mechanical dewatering processes can be significantly intensified due to the part ferrous oxidation by air with receiving more dense and heavy magnetite sludge Fe_3O_4.

Another way to increase efficiency of neutralized rinsing water clarification is its flocculation treatment [17–19].

Due to the anionic polyacrylamide with low molecular weight adding to neutralized with calcium hydroxide rinsing water it is possible to intensify ferrous hydroxide flocs sedimentation.

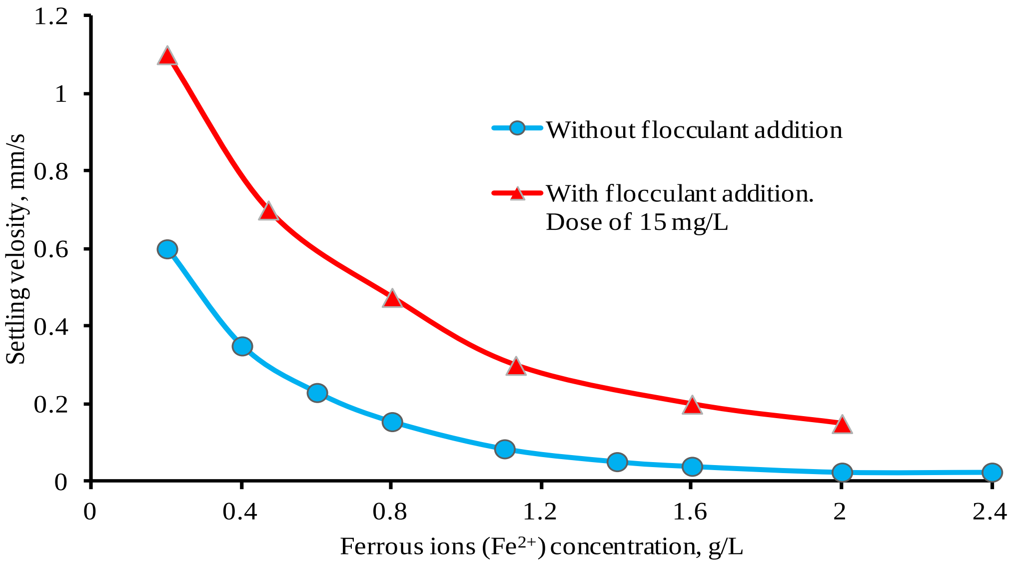


Figure 1. Effect of ferrous ions concentration on settling velocity.

For practical calculations of clarifiers the empirical formulas are offered with (1) and without (2) flocculant addition:

$$\upsilon_s = (0.47 + 2.3C_{Fe})^{-1} \quad (1)$$

$$\upsilon_s = (1.1 + 8.8C_{Fe})^{-1} \quad (2)$$

where υ_s = settling velocity, mm/s

C_{Fe} = ferrous ions (Fe^{2+}) concentration in rinsing water, g/L.

Influence of dosed anionic flocculant quantity on the settling velocity is presented in the figure 2.

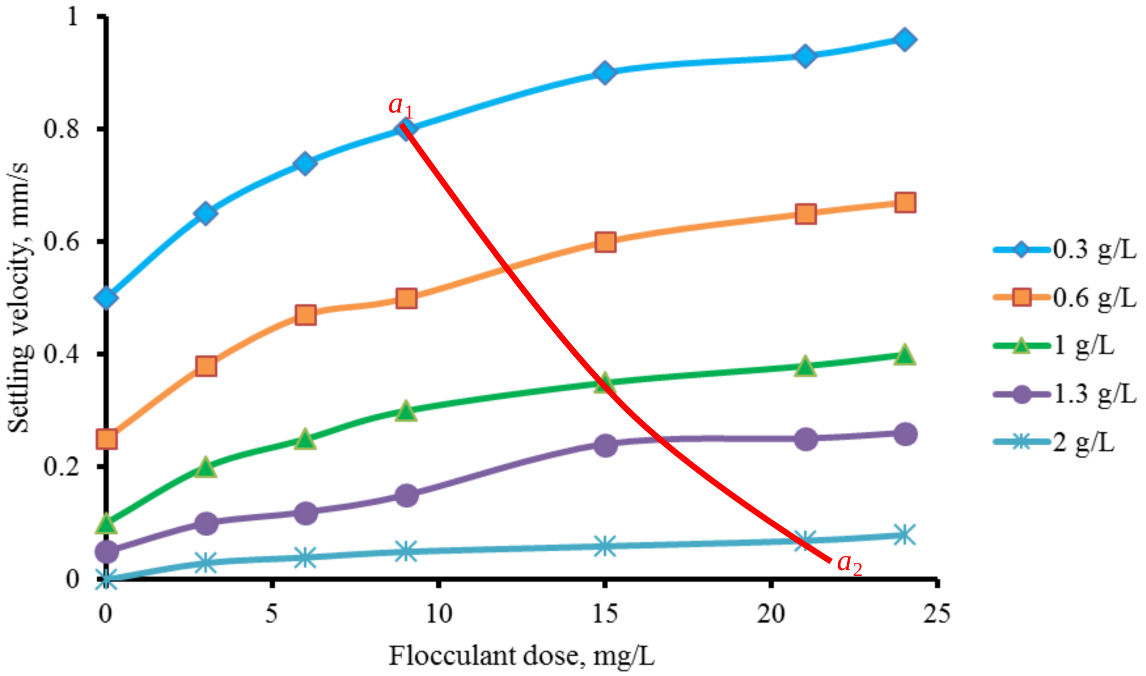


Figure 2. Effect of flocculant dose and ferrous ions (Fe^{2+}) concentration on settling velocity.

The curve a_1–a_2 demonstrates optimum quantities of the added anionic flocculant for rinsing water with various ferrous ions (Fe^{2+}) content.

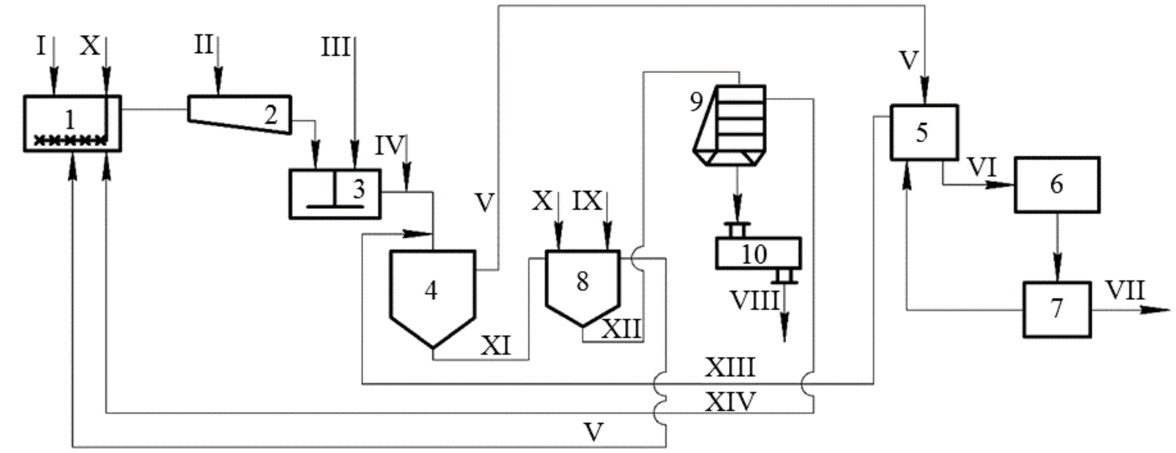
Proceeding from data presented on the figures 1 and 2, it is possible to note that use of anionic flocculant increases the flocs sedimentation speed by 2–4 times. At the same time sludge volume practically doesn't change.

Taking into account the received researches results and also forty-year successful exploitation experience of Verkh-Isetsky steelworks ZLD system [14–16] it is recommended to organize acid ferrous-containing rinsing water treatment at pickling plant as illustrated in figure 3. Acid ferrous-containing rinsing water treatment includes the following processes:

- rinsing water neutralization to pH 9–10,5 by 5 % calcium hydroxide and partial ferrous oxidation by air;
- addition of anionic flocculant and active gypsum priming to the neutralized rinsing water;
- settling of rinsing water conditioned by reagents in clarifiers;
- treatment of clarified water on deep bed sand filters.

After such treatment water will have pH=10,5–11, total hardness — 30–40 mEq/L and total alkalinity — 10–16 mEq/L. For reuse of such treated water it is necessary to adjust its salt composition. The water amount directed to further demineralization will be defined by ZLD system water salt balance.

Ferrous-containing sludge from clarifiers after oxidation by air oxygen for receiving magnetite sludge is dewatering by means of a plate-and-frame filter-presses, then dried and directed to utilization.



1 — equalization basin; 2 — mechanical mixer; 3- mechanical flocculator; 4 — clarifier; 5 — deep bed sand filter; 6 — purified water tank; 7 — pumping station; 8 — magnetite sludge receiving chamber; 9 — plate-and-chamber filter-press; 10 — cake dryer; I — rinsing water; II — calcium hydroxide; III — recirculated sludge; IV — flocculant; V — clarified water; VI — filtered water; VII — purified water directed to the demineralization; VIII — cake directed to utilization; IX – steam; X — air; XI — sludge; XII — magnetite sludge; XIII — backwash water; XIV — filter-press filtrate.

Figure 3. Process flow diagram of acid ferrous-containing rinsing water treatment.

3.2. Spent Pickling Solutions Treatment
In case of hydrochloric acid pickling spent solutions treatment can give either ferric chloride concentrate (liquid crystal) [20], which is known as recognized coagulant, or with its thermal method processing — 20–25 % hydrochloric acid solution [21, 22], which is reused at pickling plants, and as solid waste — fine iron oxide, which is easily utilized. Such technology is introduced on PJSC Severstal [23] and JSC Magnitogorsk Iron and Steel Works [24].

In case of sulfuric acid spent pickling solutions processing is implemented with receiving Ferrous sulfate ($FeSO_4 \cdot 7H_2O$), which is utilized [25, 26].

4. Conclusion
It should be noted that industrial wastewater and sludge processing technologies during the ZLD industrial wastewater systems creation are very various and depend on many factors: industrial wastewater characteristics, industrial enterprises possibilities in use of purified water, possibilities of concentrates (brines etc.) and sludges utilization at the industrial enterprises or in other organizations.

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