KRONOS ecochem®

Technical Information 3.02

Industrial Wastewater Purification with Iron Salts

Iron salts are used as precipitants and flocculants in the field of industrial wastewater purification. They are used in the form of soluble or dissolved chlorides, chloride sulfates or sulfates with bivalent or trivalent iron as the active substance.

1. KRONOS product range

Specifically for the treatment and purification of industrial wastewater, KRONOS offers bivalent and trivalent iron salt products in the form of ready-to-use solutions, wet salts with a residual moisture content or free-flowing granules.

2. Mechanisms of action of iron salts

2.1 Precipitation

Iron salts can form low-solubility compounds with a range of dissolved wastewater constituents. This process is called precipitation. All wastewater-relevant precipitation reactions are listed in Table 1.

2.2 Flocculation (primary flocculation)

The strong positive charge of the Fe^{3+} and Fe^{2+} ions leads to the discharge, coagulation and flocculation of negatively stabilised wastewater components, such as colloids, colloidally dispersed substances and suspended solids. This process is referred to as flocculation, a highly simplified diagram of which is shown in Figure 1.

Tab. 1: Precipitation reaction

Sulfide
$S^{2-} + Fe^{2+} \rightarrow FeS\downarrow$
$3S^{2-} + 2Fe^{3+} \rightarrow 2FeS\downarrow + S\downarrow$
Phosphate
$2PO_4^{3-} + 3Fe^{2+} \rightarrow Fe_3(PO_4)_2\downarrow$
$PO_4^{3-} + Fe^{3+} \rightarrow FePO_4\downarrow$
Arsenic
$AsO_4^{3-} + Fe^{3+} \rightarrow FeAsO_4\downarrow$
$AsO_3^{3-} + Fe^{3+} \rightarrow FeAsO_3\downarrow$
Cyanide
$6CN^- + 3Fe^{2+} \rightarrow Fe_2\,[Fe(CN)_6]\downarrow$
$18CN^- + 4Fe^{3+} + 3Fe^{2+} \rightarrow Fe_4\,[Fe(CN)_6]_3\downarrow$

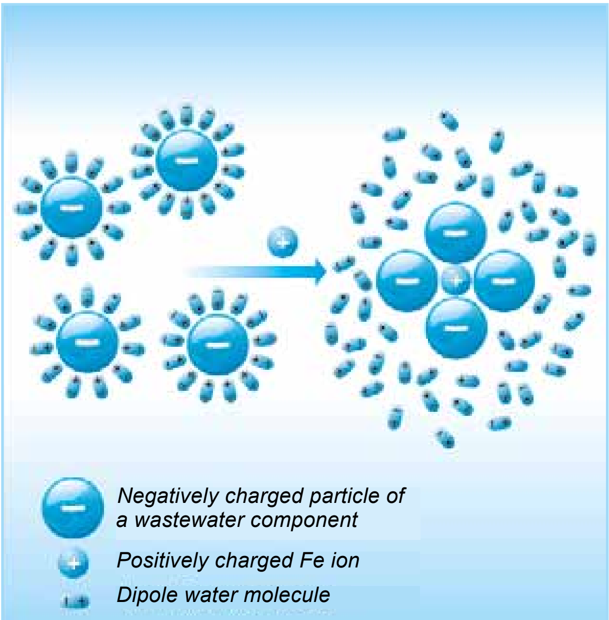


Fig. 1: Flocculation mechanism

Industrial wastewater purification

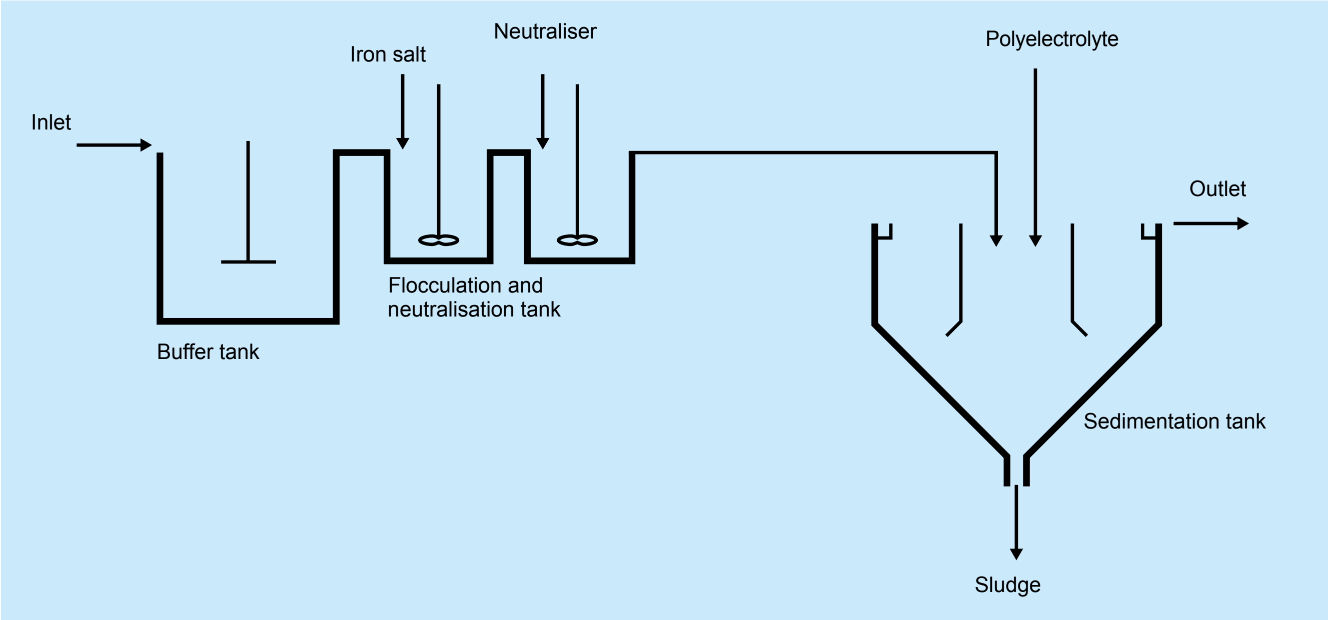


Fig. 2: Chemical-mechanical purification by precipitation and flocculation - continuous process

2.3 Hydrolysis

Iron ions are among the so-called hydrolysable metal salts, i.e. they react with water:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3H^+$$

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2\downarrow + 2H^+$$

The “excess” Fe ions are removed from the liquid phase of the wastewater by precipitation as hydroxide. Furthermore, the hydroxide flocs are capable of eliminating other wastewater components by means of adsorption and inclusion.

Hydrolysis depends on the pH-value and releases H^+ ions in the process. Hydroxide precipitation is complete when the following pH values are reached:

Fe^{3+} approx. pH 4

Fe^{2+} approx. pH 9

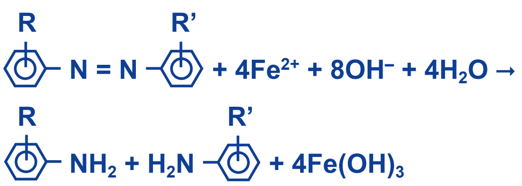
2.4 Reduction

Ferrous ions reduce chromate, which is soluble in both the acidic and the alkaline range, to form precipitable, trivalent chromium hydroxide:

$$CrO_4^{2-} + 3Fe^{2+} + 8H^+ \rightarrow Cr^{3+} + 3Fe^{3+} + 4H_2O$$

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3\downarrow$$

Textile wastewater containing azo dyes can be decoloured by means of reductive precipitation using bivalent iron salts (see TI 3.03):



3. Chemical-mechanical purification by precipitation and flocculation

The physicochemical processes described in Section 2 are all aimed at converting dissolved or very finely dispersed wastewater constituents into a form which can be mechanically separated. The actual purification of the wastewater does not take place until the solids are subsequently separated from the liquid.

The process as a whole is referred to as chemical-mechanical purification by precipitation and flocculation.

3.1 The continuous process

Chemical-mechanical wastewater purification with iron salts is broken down into three process steps:

- Collection of the raw wastewater
- Chemical treatment
- Mechanical solid/liquid separation

Figure 2 shows a diagram of the process, which can be described as follows:

Wastewater is collected in a tank and equalised in terms of quantity, temperature and composition. Aeration may be necessary in this context.

In the first mixing stage, iron salt solution is added to the process under a high energy input. This is where all primary flocculation processes take place.

The pH-value drops to about 3, depending on the required added quantity, buffer capacity and initial pH-value.

In the second mixing stage, the wastewater is neutralised, preferably with milk of lime. Equally good mixing conditions should also prevail here and the pH values should be above 7.

The third chemical stage involves the addition of polyelectrolyte with as little energy input as possible. As a

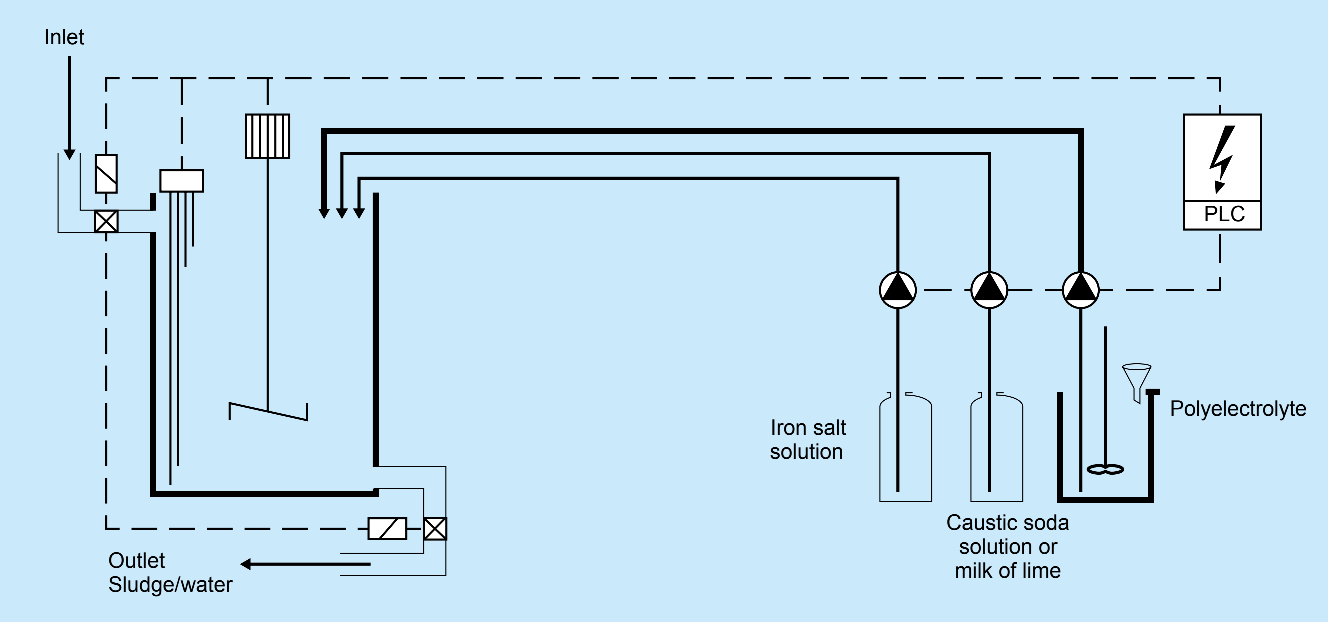


Fig. 3: Chemical-mechanical purification by precipitation and flocculation - batch process

flocculation aid, the anionic polyelectrolyte causes an increase in the size of the flocs and is designed to accelerate sedimentation (secondary flocculation).

The chemically treated wastewater is transferred to a sedimentation hopper, preferably designed as a sludge contact tank, to mechanically separate solids from the liquid. Alternatively, a lamella clarifier or lamella separator can also be used. The solids can also be separated by means of the flotation method.

3.2 The batch process

The continuous process shown in Figure 2 presupposes a relatively high wastewater flow rate. However, if the wastewater flow rate is low and very irregular, discontinuous wastewater purification using the batch process is more suitable (Fig. 3). In principle, all that is needed for this purpose in terms of equipment is a single tank that serves consecutively as a collecting, mixing and sedimentation unit. With a PLC program and associated contact switches, the individual process steps can be automated to such an extent that only little manual intervention is required and a virtually continuous process can be achieved.

3.3. Laboratory tests

The discontinuous process can be simulated fairly accurately on a laboratory scale. The type, quantity and combination of chemicals can be determined in a beaker, as can the attainable purification effect. Generally speaking, it must be kept in mind that chemical-mechanical purification by means of precipitation and flocculation has an only limited performance range. Wastewater components that cannot be precipitated or flocculated, such as water-soluble alcohols, cannot be eliminated.

4. Fields of application of chemical-mechanical purification by precipitation and flocculation

Chemical-mechanical purification by precipitation and flocculation is used in many industrial sectors as a stand-alone process, as one stage in combination with other processes, or as a preliminary stage to biological wastewater treatment.

4.1 Emulsion cracking

The flocculation of emulsified wastewater components is referred to as emulsion cracking. This process is most commonly used to purify wastewater in the paint and paint-processing industries. Wherever plastic emulsions are manufactured, transported and processed, the “rinse water” needs to be cracked. The importance of this wastewater purification process is increasing as a result of the progressive conversion of paints, coatings and adhesives to solvent-free, waterborne systems.

All wastewater containing emulsified oils and fats can be purified by means of emulsion cracking with iron salts. This process is used particularly frequently in the field of metalworking to purify wastewater containing cutting and drilling oil, and in the oil refinery sector.

In the foodstuffs industry, wastewater containing fats and proteins is “cracked” and subsequently purified by mechanical means, preferably using the flotation method.

4.2 Suspension flocculation

Wastewater components that contaminate the water in the form of suspended or finely dispersed solids are rendered mechanically precipitable by a method known as suspension flocculation.

The use of suspension flocculation with iron salts is particularly widespread in the ceramics, chemical and paper industries. Wastewater from flue-gas purification processes, e.g. ash washings from power stations, is also purified by means of chemical-mechanical wastewater purification processes.

Another field of application is the purification of wastewater from bottle washing plants in the beverage industry..

4.3 Decolouration

Wastewater from the textile finishing industry often contains highly stable dye residues, which are resistant to practically all common purification processes.

However, the use of reductive precipitation with ferrous salts and lime (Section 2.4) makes it possible to permanently decolour the wastewater

4.4 Sulfide precipitation

The wastewater from tanneries (liming water) and oil refineries contains sulfides and hydrogen sulfide (H_2S). Furthermore, sulfides can also be formed by anaerobic processes in wastewater from the foodstuffs industry. These sulfides can be precipitated by the use of both ferrous and ferric salts (Table 1). Problems with odour, corrosion and poisoning can be controlled by this method.

4.5 Chromate detoxification

The use of ferrous salts makes it possible to reduce highly toxic chromate into precipitable chromium(III). Subsequent neutralization or hydrolysis precipitates insoluble chromium(III) and ferric hydroxide, which can then be removed from the wastewater mechanically.

Chromate detoxification or reduction is used in the cement processing and metal surface finishing industries.

4.6 Other fields of application

In addition to the five primary applications described, iron salts are also used in other fields of application.

4.6.1 Phosphate elimination

The classic field of phosphate elimination is the purification of municipal sewage. But phosphate even is added to many kinds of industrial wastewater which are purified biologically.

However, some wastewater from the chemical, foodstuffs and beverages industries contains so much phosphate that selective phosphate elimination is carried out with iron salts (see TI 3.01).

4.6.2 Arsenic elimination

Wastewater from ore dressing and metallurgical ore processing plants, as well as mine drainage water and seepage water (contaminated sites), can contain arsenic. Iron salts precipitate arsenic to form hardly soluble iron arsenites and arsenates. In special cases, this precipitation process is also used for arsenic elimination in the treatment of drinking water and process water.

4.6.3 Cyanide detoxification

The precipitation of toxic CN^- ions with iron salts is a time-honoured method. This process leads to the formation of hardly soluble “Prussian blue” or “Berlin white”, depending on the conditions and the iron salt selected. It is particularly suitable as a coarse purification process prior to detoxification by oxidation. It is predominantly used to treat effluent concentrates in the surface finishing industry, or also in soil decontamination.

4.6.4 Heavy metal precipitation

Iron salts are incapable of precipitating heavy metals directly. However, this process is still used with success. The elimination effect is achieved through adsorption and inclusion processes by the hydroxide flocs. The most familiar field of application is the purification of wastewater from flue gas desulfurisation plants by means of precipitation and flocculation with ferric salts.

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