# Use of metallurgical scale in the processes of engineering protection of the environment

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The main directions of alternative use of scale, a metal-containing waste material from forging and pressing shops at metallurgical enterprises, were suggested and researched within the framework of this work. Scale composition from the processes of heat treatment and forging of steel components from forging and pressing shops at the machine-building plant in the Moscow region was examined. It was established that up to 99 % of scale is presented by magnetic phases of iron oxides, supposedly in the form of $Fe_3O_4$, and alloying components do not practically transit in scale. The technology of sulfuric acid and hydrochloric scale processing with obtain of coagulants is suggested for purification of waste water at galvanic sections or hydrochloric pickling solutions respectively. The technology of scale use as filtrating loading for the processes of purification and neutralization of chromium-containing waste water is proposed. Hugh reducing ability of scale as a reactant for purification of acidic waste water was established in the wide range of initial concentration values of chromium (VI) compounds. Possibility of scale use as Fe-containing additive for pyrometallurgical processing of quartzite-leucoxene, a large-capacity titanium-containing mineral waste, was examined. It was established that chemically active pseudobrookite is the final conversion product; it can be used as raw material for manufacture of wide spectrum of commercial products.
***Key words:*** scale, processing, forging and pressing shop, recycling, pseudobrookite, pickling solution, chromium (VI) reduction.
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## Introduction

"Green industry" becomes a new trend providing realization of the sustainable development concept. Most of the countries take into account the principles of "green production" during development of the new technologies of plant construction [1].

Creation of the new power- and resource-saving technologies, minimization of negative effect on the environment, development of the new high-efficient technologies of water and gas purification are those directions that are strictly required for existence of each modern enterprise. Organization of low-waste production within the framework of economical concept of closed circuit is the most complicated and most important part of "green industry" [2].

Metallurgical industry is one of the largest sources of forming of substantial volumes of large-capacity mineral wastes with various compositions. Mining processes, hydro- and pyrometallurgical technological stages, melting and metal forming processes, application of galvanic coatings make only the short list of the most waste generating processes [3-5].

Metallurgical scale is a waste material of forging, stamping and heat treatment processes for metallic products, it forms during operation of forging and pressing shops. The volumes of scale forming make 20-30 kg per 1 ton of finished product in average [6], what is equivalent to 800-900 kg per day for a relatively small forging and pressing shop at a machine-building enterprise in the Moscow region. Total volume of forming scale is transferred to slag dumping works for permanent location and is not used again. According to the passport of the Federal classification catalogue of wastes, scale is related to the 4th danger class and is subjected to mandatory payment as large as 716 rub/t (within the framework of agreed standard regulation of forming of wastes and limits for their location) or about 17,900 rub/t in the case of excess of the established limit.

Melting can be considered as the most widely distributed method of scale processing, however, according to the regulation documents [7, 8], scale from the forging and pressing shops is suitable only for blast furnaces, which are presented in limited number and accompanying essential logistic expenses are often not profitable for an enterprise. Overwhelming majority of works devoted to scale processing describe granulation processes (manufacture of pellets) and briquetting, that really are preparing operations before pyrometallurgical processing [9-13]. Several scientific teams propose to use scale as additive to building materials [14-18]. Some enterprises try to solve the problem of scale processing and utilization via its use for perimeter pavement of domestic roads or as substrate / filling agent in building works; however, it is not always allowable from the point of view of ecological and industrial safety.

The main aim of this work was examination of possibility of using scale from the processes of heat treatment and forging in forging and pressing shops as a secondary resource for manufacture of different products for metallurgical industry.

## Materials and methods of research

Examination of phase composition was carried out on X-ray diffractometer DRON-3 M (Russia).

Content of metals in scale and processing products was measured via the wet chemistry method (acidic / alkali dissolution) with consequent identification of composition of solutions (i.e. other liquid processing products) on atomic emission spectrometer with magnetic plasma “Spektroskay” (Russia) [19].

Content of chromium (VI) ions was determined in photometric mode on compact spectrophotometer DR 2800 (HACH USA).

The following samples of substances were used for the experiments:

1. Processed pickling solution from the section of galvanic coatings application (the mix of sulfuric and hydrochloric acids) from the machine-building enterprise in the Moscow region.
2. Processed acidic solutions and waste waters from chromium plating process of steel components.
3. Scale from the processes of heat treatment and forging of 08Kh18N10 austenite steel from a forging and pressing shop at a machine-building enterprise in the Moscow region.
4. Quartzite-leucoxene (titanium-containing) concentrate from Yarega oil-titanium deposit.

The following processes were suggested as alternative directions of scale processing after heat treatment:

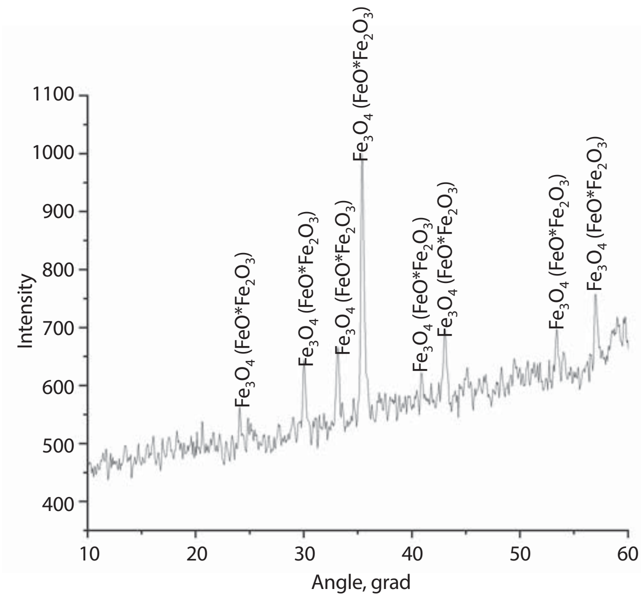


**Fig. 1. Diffraction pattern of the scale sample**

1. Obtaining of pickling solutions on the base of Fe chloride. This process is based on the interaction reaction between 20-25 % hydrochloric acid and scale, it was carried out with scale / solution phase relationship 1:10 at the boiling temperature of this solution

$$Fe_3O_4\,(FeO{*}Fe_2O_3) + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 4H_2O \quad (1)$$

2. Obtaining of Fe-containing coagulants as a result of interaction between high active oxides and processed solutions of 30-35 % sulfuric acid. Processing was similar to the reactions with hydrochloric acid

$$Fe_3O_4\,(FeO{*}Fe_2O_3) + 4H_2SO_4 \rightarrow FeSO_4 + Fe_2(SO_4)_3 + 4H_2O \quad (2)$$

3. Decontamination of chromium-containing solutions via reduction of chromium (VI) in chromium (III) compounds during passing the solution through scale charging. Acid neutralization process with deposition of hardly soluble Fe and Cr compounds takes place in parallel mode.

$$6\,Fe_3O_4\,(FeO{*}Fe_2O_3) + K_2Cr_2O_7 + 31\,H_2SO_4 \rightarrow \rightarrow 9\,Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 31\,H_2O \quad (3)$$

4. Use as activating additive for pyrometallurgical processing of quartzite-leucoxene with obtaining chemically active titanium-containing mineral pseudobrookite [20].

$$2\,Fe_3O_4\,(FeO{*}Fe_2O_3) + 0.5\,O_2 + 3\,TiO_2{*}SiO_2 \rightarrow \rightarrow 3\,Fe_2TiO_5 + 3\,SiO_2 \quad (4)$$

## Results and discussion

Composition of scale sample taken from steel forging within the temperature range 1180 °C – 900 °C was examined at the first stage of the research. Phase composition of the sample is presented on the diffraction pattern (**Fig. 1**) and elementary composition – in the **Table 1**.

Based on the data from the diffraction pattern (see Fig. 1), it can be seen that overwhelming part of scale has composition presented by the mixture of Fe (II) and Fe (III) oxides, and it is impossible to extract the dominating phase due to close interplane distances. Chemical analysis of scale displayed that only small part of alloying components transferred to scale during heat treatment and forging.

Transition of separate components from scale to acidic solutions should be provided for obtaining of iron chloride or other Fe-containing coagulants. The data about degree of scale dissolution in solutions depending on processing time are presented on the **Fig. 2**.

The Fig. 2 testifies that hydrochloric acid reacts with scale rather more intensively (due to forming of iron chlorides and their secondary reaction with scale); in this case the time of maximal transition of the components in the solution is lower by 30 % in average that in the case of use of sulfuric

Table 1. **Elementary composition of the scale after steel heat treatment, %**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Steel 08Kh18N10 | Si | Mn | Ni | Cr | Ti | Cu | Fe |
| | 0.71 | 0.18 | 10.4 | 18.9 | 0.45 | 0.29 | 69.07 |
| Scale | $SiO_2$ | MnO | NiO | $Cr_2O_3$ | $TiO_2$ | CuO | $Fe_3O_4$ |
| | 0.45 | 0.09 | 0.20 | 0.24 | 0.05 | 0.13 | 98.84 |

acid. Chemical composition of obtained solutions is shown in the **Table 2**.

Where A is anion $(SO_4)^{2-}$ for sulfuric acid and anion Cl- for hydrochloric acid

The data of Fig. 2 and Table 2 are compared and it can be seen that iron (up to 99 %), nickel, manganese and copper transfer in the solution quantitatively, at the same time titanium and chromium compounds practically don't dissolve and completely remain in sediment. Filtered and washed sediment can be used as chromium-titanium raw material.

Hydrochloric solutions are directed to the stage of $FeCl_2$ deoxidation in $FeCl_3$ form via chlorination or oxidation by oxygen [21, 22]. In this case, according to the data of economical evaluation, the coat of iron chloride obtaining through the suggested technology will be lower in average by 40 %, both owing to cheap raw materials and decrease of chlorine consumption for oxidation via reactions (5) and (6).

$$Fe + Cl_2 \rightarrow FeCl_2 \quad (5)$$

$$2\,FeCl_2 + Cl_2 \rightarrow 2FeCl_3 \quad (6)$$

The mixture of Fe (II) and Fe (III) sulfates, which was obtained during use of worked pickling solutions, can be used as a high-efficient coagulant both for purification of galvanic drains (i.e. from chromium (VI) ions) and for purification of any other waste waters (cooling, washing, hydro-cleaning etc.). This mixture of two salts will make a positive synergetic effect [23, 24] and will allow to increase efficiency of coagulating purification. Presence of micro-impurities of nickel, copper and manganese compounds will not influence on purification quality of waste waters.

In order to evaluate possibility of scale use as reducing reactant of chromium (VI) compounds from preliminarily comminuted material with 0.5-1.0 mm coarseness, a flowing filtering cartridge with cross section square 2.5 cm² and height of layer 20 cm was assembled. Chromium-containing waste waters with various content of chromium (VI) ions were passed through this cartridge with permanent volumetric consumption 1.0 l/h and linear speed 4 m/h. Passed solution was neutralized by sodium hydroxide with deposition of non-soluble chromium (III) hydroxide and then analyzed for residual content of chromium (VI) ions. The data about influence of content of chromium compounds in waste waters on degree of Cr (VI) → Cr (III) conversion are presented on the **Fig. 3**.

The data of the Fig. 3 testify that passing of even strongly contaminated chromium-containing waste waters through filtering loading of scale makes it possible to transfer chromium (VI) compounds in not so dangerous and easily extracting chromium (III) form with high efficiency. Partial neutralization occurs due to conducting interacting reactions between oxides and acid, and pH of the system rises. In the case of increase of a filtering cartridge size, this technology can be used even for decontamination of worked chromium-containing electrolytes.

Evaluation of possibility of scale use in processing of large-capacity "wastes" of development of oil-bearing sands (quartzite-leucoxene tailings) via the above-described pyrometallurgical processing technology [20] was the finished experimental stage. Quartzite-leucoxene is a valuable titanium-bearing raw material, however, there is not any profitable and relatively reliable technology for its processing among many variants [25-28]. The technology of pyrometallurgical processing with use of scale, which is suggested by the authors, will allow to solve the problem of utilization of just two large-capacity mineral wastes.

Scale was preliminarily comminuted (to the size 40-72 µm) and then mixed with quartzite-leucoxene in equi-molar amounts and subjected to pyrometallurgical processing according to the reaction (4) during 5 hours at the temperature 1450 °C. This research was aimed on evaluation of principal possibility of replacing pure oxides by scale with forming of chemically active phase of pseudobrookite. The data on phase composition of the obtained sample are presented on the diffraction pattern (**Fig. 4**).

It can be seen from this Fig. 4 that high-active pseudobrookite phase can be formed in the process of scale and quartzite-leucoxene sintering. Degree of quartzite-leucoxene → pseudobrookite conversion exceeds 90 % in use as additive of metallurgical scale. The obtained mineral (pseudobrookite) reacts intensively with sulfuric acid solutions

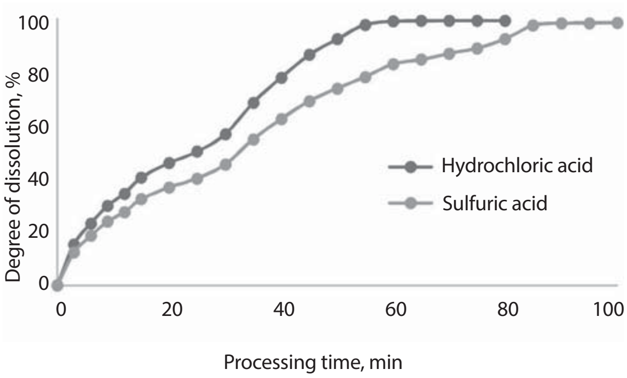


**Fig. 2. Degree of scale dissolution in acidic media**

Table 2. **Chemical composition of solutions**

| | Salt content, g/l | | | | | | | I.e. in the form of | |
|---|---|---|---|---|---|---|---|---|---|
| | $Si(OH)_4$ | $Mn_XA_Y$ | $Ni_XA_Y$ | $Cr_XA_Y$ | $TiO_XA_Y$ | $Cu_XA_Y$ | $Fe_XA_Y$ | $Fe^{2+}$,% | $Fe^{3+}$,% |
| Sulfuric acid | 0.1 | 0.186 | 0.392 | 0.009 | 0.014 | 0.242 | 234.70 | 31 | 69 |
| Hydrochloric acid | 0.1 | 0.155 | 0.329 | 0.013 | 0.015 | 0.204 | 192.18 | | |

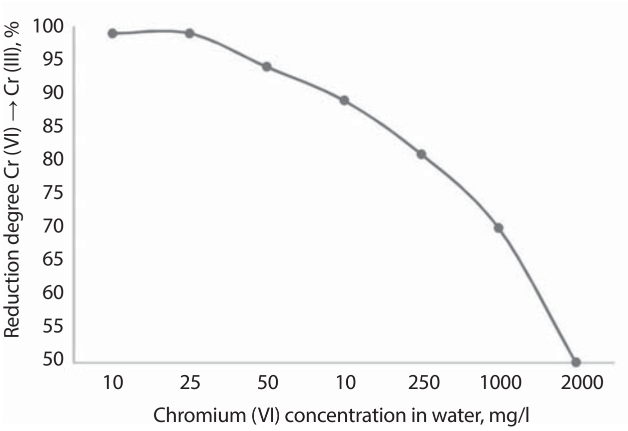


**Fig. 3. Influence of initial chromium (VI) concentration on reduction Cr (VI) → Cr (III)**

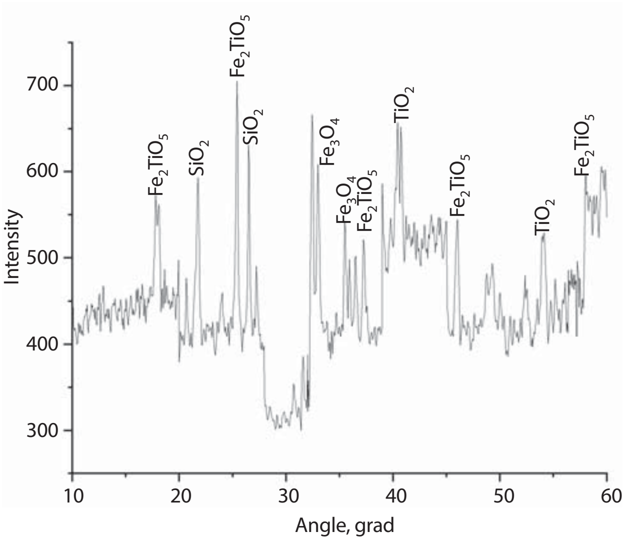


**Fig. 4. Diffraction pattern of the sample after pyrometallurgical processing of quartzite-leucoxene and scale**

of various concentration and can be used for obtaining of titanium dioxide, titanium salts as well as complex titanium-containing coagulants [29-31].

## Conclusions

Based on the researches presented in this work, it is possible to note alternative directions of use of scale from heat treatment and forging of steels.

Scale can be an excellent raw material for obtaining pickling solutions on the base of Fe chloride; in this case replacement of metallic iron by scale allows not only to decrease chlorine consumption, but also to refuse from use of pure iron or scrap, which can be subjected to remelting in a usual electric arc furnace without reduction processes, unlike scale.

Sulfuric acid Fe-containing solutions can be used as high-efficient coagulants for purification of industrial waste waters and, particularly, galvanic drains. In this case presence of two Fe salts with different oxidation degrees in the solution will additionally strengthen coagulating activity of reactant.

Use of scale as filtering material will allow to provide high-efficient decontamination of chromium-containing waste waters; it will be accompanied by the process of neutralization of free acid.

Pyrometallurgical processing of quartzite-leucoxene with obtaining high active titanium-containing mineral (pseudobrookite) can be suggested as one more direction for scale use. Pseudobrookite, in its turn, can be processed via the standard sulfuric acid technology in commercial titanium compounds (sulfate, oxide) or high-efficient complex titanium-containing coagulant.

Presented technologies will let us not only to decrease substantially the volumes of metallurgical wastes which are located for permanent storage within the framework of realization of the concept of low-waste production, but also to prevent negative effect from a wastes storage site on the environment. The mentioned directions of alternative use of scale from heat treatment and forging processes will allow to decrease ecological payments and to increase profitability of production process.

Potential economical efficiency for the enterprise can be presented as follows:

1. Decrease of ecological payments for negative effect on the environment by 716 rub/t of scale (in the case when the standard regulation 17,900 rub/t is exceeded).
2. Lowering of expenses for purification of waste waters at the enterprise in average by 25-30 thousand rub/month (decrease of volumes of coagulant purchase).
3. Reduce of penalty sanctions for above-limit emission of contaminating substances in municipal and storm water drainage (first of all for chromium (VI)), refuse of purchase of reducing reactants – up to 75-90 thousand rub/month.
4. Realization (internal use) of reduced pickling solutions – 5-8 thousand rub/t.
5. Sale of scale as raw material for pyrometallurgical processing of quartzite-leucoxene – 2-4 thousand rub/t.

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