Obtaining of an iron powder from spent pickling solution

Kargin J.[1], Mukhambetov D.[2], Biseken A.[3]

Получение железного порошка из отработанного травильного раствора

Каргин Д. Б.[1], Мухамбетов Д. Г.[2], Бисекен А. Б.[3]

[1]Каргин Джумат Бейсембекович / Kargin Jumat Beysembekovich – директор,
Департамент коммерциализации технологий,
Евразийский национальный университет имени Л. Н. Гумилева, г. Астана;
[2]Мухамбетов Даут Галимжанович / Mukhambetov Daut Galimszanovich – профессор,
кафедра информационных систем,
Алматинская академия экономики и статистики;
[3]Бисекен Агарыс Балгерейулы / Biseken Agarys Balgereyuly – доцент,
кафедра электроснабжения промышленных предприятий,
Алматинский университет энергетики и связи, г. Алматы, Республика Казахстан

Abstract: *the report examines the technical possibility and economic feasibility of producing ultrafine iron powders from the spent pickling solution in industrial production conditions of unalloyed steels.*
Аннотация: *в докладе рассматриваются техническая возможность и экономическая целесообразность получения ультрадисперсных порошков железа из отработанного травильного раствора в условиях промышленного производства нелегированных сталей.*

Keywords*: unalloyed steel, waste pickle liquor, spent pickling solution, rolling scale, iron nanopowder, reduction of iron oxides.*
Ключевые слова: *нелегированная сталь, отработанный травильный раствор, прокатная окалина, нанопорошок железа, восстановление оксидов железа.*

In the steel industry a hot rolled steel requires pre-treatment before undergoing various other processes like cold rolling, deposition of protective coatings, etc. This pre-treatment is aimed to remove various oxide layers, rust or scale and other impurities from the steel surface by passing the steel strips through the vessel with pickle liquor. The pickling process generates large amount of pickling sludge which contains acidic rinse water, dissolved metal salts of iron, iron chloride and spent acid. The spent pickle liquor is a hazardous waste therefore it should be treated.

In this report we considered the treatment of spent pickle liquor, a regeneration of used acid and utilization of a waste sludge. Particular attention was paid to the obtaining of iron powder from spent pickling solution.

Let us consider the production of unalloyed steel. Unalloyed steel has no elements added to the steel during smelting. It contains only natural impurities except deoxidants therefore is the purest among other steels. Production of alloy steel comprises the following main steps: melting and casting of steel into ingots; rolling of ingots into slabs; hot rolling of slabs into strips; welding and coiling of strips; pickling in hydrochloric acid; the first cold rolling; annealing of rolls in bell-type furnaces; the second cold rolling.

Layer of oxides or scale on steel surface arises during the hot working processes. Hot rolling is a process in which steel is treated above its recrystallization temperature around 600-700 ^{0}C. At these temperatures on the steel surface usually arises the thick oxide layers and scale which must be removed for subsequent processing of steel strip. Therefore steel goes through a unit process called pickling to remove these impurities and stains from the surface of steel strips [1].

The initial stages of the etching process are the separation of the oxide layer from the steel strip by dissolving it in hydrochloric acid. Scale on the steel surface consists of wustite, magnetite and hematite. Directly to the metal adjoins the layer of wustite (up to half of the total scale thickness), the outer layer is a hematite (up to 10% of the thickness of the layer of magnetite is located between them. The most dense is a layer of hematite, which creates a major difficulty in the release of hot-rolled strips of scale. Pickling is a process which consists of chemical removal of scale (surface oxides) and other dirt from steel by immersion in aqueous acid solution. The basic components of oxide interact with the hydrochloric acid with the formation of iron chlorides [2].

At steel manufacturing is generally used continuous strip pickler (CSP). Etching of the strip surface produced in successive baths (normally from three to five). In this case so-called mother acid solution is poured into the last bath in the course of the strip movement, and then it flows by gravity to each subsequent bath, gradually losing the acid concentration. The product of acid reaction with oxide scale - ferric chloride easily dissolves in water, which makes it possible full regeneration of spent solutions without accumulation of the insoluble residues. The sludge that is formed from dross residues, precipitates and is removed by washing of baths and strip surface. The spent etching solution is supplied to the warehouse of the solutions [3].

Further the spent solution from the warehouse by means of a pneumatic pump enters through the filter in the heat exchanger of the regeneration installation in which the solution is heated to 92-94 ^{0}C. The heated solution is fed into the reactor. The reactor is a steel tower, lined with refractory bricks heated by four gas burners. The spent solution is pumped through the spray nozzles, is heated to a temperature 600 ^{0}C and dissolved therein ferrous chloride $FeCl_2$ thermally decomposes to fine гематит Fe_20_3 and hydrogen chloride gas in accordance with the reaction $4FeCl_2 + 4H_2O + O_2 = 2F_2O_3 + 8HCl.$

Powdered hematite is separated in the cyclones from the exhaust gases and poured into the bottom of the reactor, and there from flows into the hopper for loading powders in a dosage plate. Iron oxide is shipped in powder form or as granules. The steel plant it is usually used directly in sinter plants [3].

The oxide powder produced from rolling scale, is a valuable material for use in various branches of science and the national economy but we propose to continue the processing of the oxide powder by its reduction to iron powder as the next stage of treatment of rolling scale in the line of continuous strip pickler (CSP). It is known that iron powder obtained by reduction from oxide powder on non-alloy steel has high purity and increased cost. The market price of rolling scale is about $ 0.06/kg, of ordinary iron powder is $ 0,8/kg, i.e., 13 times more expensive [4].

The identified regularities of oxide film growth and its transition to the scale on the surface of unalloyed steels may serve as a scientific basis for the development of a new method for producing iron oxide nanoparticles by surface oxidation of such steels [4, 5]. We conducted a reduction of the iron oxide obtained from the spent etching solution in a stream of hydrogen at a temperature of 400-500 ^{0}C. XRD results showed that the resulting powder is pure iron. Measurements on raster SEM JSM-5910 electron microscope showed that the reduced iron particles have a shape close to spherical. Specific surface of reduced iron powder was S_{sp} = 9.2 m^2 / g, and the calculated average particle diameter was 83 nm, which corresponds to the dimensional criteria of nanoparticles [6].

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