SUPERIOR WASTE RECOVERY IN THE METALLURGICAL INDUSTRY

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Abstract: On the global scale the generating rhythm of the scraps exceeds the natural assimilating capacity of the most regional ecosystems.

The numerous studies mode about the good "practices" spotlighted the succe of the ecological technologie, but expoed the exitence of many indutrial ineficient, polluant and dangerous installation too, wich are, still, into operation. To the last evaluation, the industrialized countries should cut down to minimum four times the row material consumation, so that the considerable effort are necessaryto decrease the quantities of scraps resulted in the industrial processes and increase their recirculation.

A "clean" technology could rely on a new, less polluted production procedure, that recirculates the resulted scraps in a certain phase of fabrication or, on the utilization procedure of the scraps becoming raw material for a secondary production.

The conception of the scraps recovery and recirculation should be brought up to date emphasizing the management and the marketing activities to find the utilization fields of the accumulated scraps in the industrial dump – yards.

Keywords: *scraps, metallurgical sources, metallic slags, metallic powders*

1. Scraps Sources from the Metallurgical Plants

In the frame work of the technological flours, typical to the iron and steel industries, besides main products the important quantities of the by – products and scraps outcome. In generally, the by – products are re – introduced in the technological flow, boving high degree of utilization.

The scraps are stored on the particularly fited out surfaces but, at present, the recirculating of such materials is pursued by the nonpolluted technologies as possible.

A classification of such scraps has in view the following criteria:

-the content of the certain chemical elements, depending on the technological process from which they proceeded;

-risk degree related to the environment and health impact;

-aggregation state at generation moment ; the intinsic value of the scrap and its utilization possibility;

-generation sources (technological flow and operation which generated the scraps).The main scrap generating sources from metallurgical fields are: coke – chemical plants, sintering, Blast – furnaces plants, Steelworks, Rolling Mils, Forging – plants, Thermal – treatments shops, Mechanical processing – works and their types of scraps are: powders, sludge (slurry), slags, refractory debris chips (splinters), scales, etc. For example, from rolling mills the scraps which the following characteristics resulted (tables 1, 2):

Table 1 *Average grain – size of the scale, slag and metallic melting.*

Scrap type	Grain size (mm)					
	0…1	1…5	5…10	1…15	15…20	>20
Scale (%)	8.24	25.06	28.72	32.78	4.80	-
Metallic slag (%)	7.14	9.22	7.15	9.50	31.85	33.30
Metallic melting (%)	-	3.6	4.72	11.78	10.62	68.78
Sludge scale (%)	71.4	28.50	-	-	-	-

Table 2 *Chemical composition of the metallic scraps*

Scrap type	Chemical composition (%)			
	Fe	SiO_2	CaO	Mn
Scale (%)	66.97 – 71.23	0.70 – 1.97	0.36 – 1.47	-
Metallic slag (%)	63.66 – 70.16	0.11 – 1.46	1.14 – 1.52	0.42 – 0.8
Metallic melting (%)	74.48 – 78.37	0.30 – 0.45	1.08 – 1.35	0.43 – 1.13

Having in view the high iron quantity of such scraps, their higher valorification was layed on the table, aiming to the iron extraction and its use in other fields.

One of the up-to-date valorification method of ferrous scraps is the powder getting used for small parts manufacturing, with complex geometry, of which fabrication, by casting, isn't profitable from technical and economical point of view, or parts manufacturing which, by their operation nature, should have a porous structure (filters, self-lubrication bearings, porous plates for accumulators etc.).

At present, the utilization methods of the metallic powder-scraps should answer to the following questions:

-getting of the acceptable purity powders for those fields where they will be used;

-achievement of the wished phisical (shape, grain-size etc) and technological characteristics (compression, sintering capacity)

-acceptable cast of the row materials; resources availability; value of the processing investments.

A large range of the products manufactured by the typical methods of the powders metallurgy is that of the iron and steel products with higher characteristics, used for mechanical engineering, welding rods (electrodes), electromagnetical couplings, sintered bearings, et.

Generally, the powders, necessary to these items manufacturing, are gotten from the oxides resulted from metallurgical and chemical process, and they are pure products; their purity degree and shape and grain-size depending on the fabrication method.

The scraps resulted from the parts and tools manufacturing as well as scraps of the plastic deformation are recovered by the alloyed melting spraying (pulverization) or by the mixing of the pure metal powders in the given ratio.

First procedure shows the draw hack of the spherical grain-size powder getting good for the cases where the required porosity parts are necessary only and that of the contamination by the melt contact to the furnace refractories.

The second procedure supposes the pure metallic powder manufacturing, powders, that, not in all cases, could be gotten with the necessary characteristics and either in convenient economical conditions.

Manufacturing of the alloyed powders, in the advanced homogeneity and convenient economical conditions, on the electrochemical way, removes the above mentioned, drawbacks.

Complying with this technology, the anodic dissolution of the respective alloy takes place from semi-finished or worn out parts, in an electrolyte of sodium or amonium chloride aqueous solution, having concentration of 20%, voltage 12-24V, current density 0.01A/dm^2

Formation of the metallic hydroxides takes place, which are washed, filtered and dewatered in air or nitrogen.

The gotten metallic oxides are reduced by hydrogen at temperature between 500-1000°C with or without final crushing.

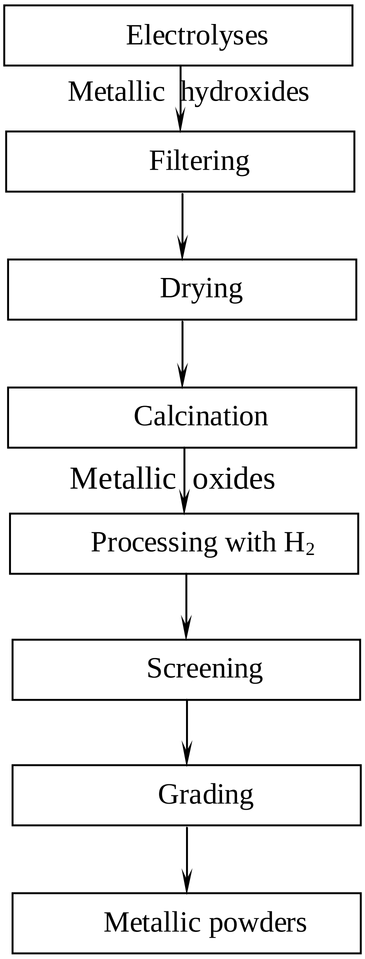
To get powders from high alloyed steels, the anode is made of the worn out tools or scraps resulted from the respective steel-grade tools fabrication. The cathode is made of copper, nickel or graphite. The gotten powder is screened, graded and mixed up with graphite powder additions to achieve, finally, the necessary carbon content.

The powder is pressed in plates and sintered, afterwards.

By same technology the non-alloyed metallic powders could be gotten using pure metallic anodes and electrolyte consisting of the aqueous solution of pure amonium chloride, the powder purity being some to that of the anode (purity).

The cathode could be same metal (alloy) as the anode: copper or graphite.

Technological steps :



The chemical composition of the gotten powder is same as that of the anode and the grain –size is polyhedronical shape. Grain-size is direct variable to the current density.

By these technologies the followings are gotten

1) The alloyed powders, for every part of the mechanical engineering, made in the technological flaw: pressing, sintering; as well as every tool, using the worn-out parts and tools and, also, by the valorification of the scraps resulted from the fabrication process of the parts, tools, rolled, forged, extruded – and cast semi-finished products.

2) The non-alloyed powders of high purity metals, the powder purity being same as to that of the anode.

3) The scraps, as stainless steel chips, could be changed in powders using the intercrystalline corrosion method. For that it should be started from the material with higher carbides precipitated on the crystalline grain-size borders, in order that the intercrystalline corrosion process to be developed quickly. This method uses the austenitic stainless steel chips proceeded from the mechanical processing.

Several thermal treatments are used to precipitate the carbides of the grain size borders and to sensitive the steel at the intercrystalline corrosion:

- first treatment is quenching in solution consisting in steel heating at temperatures ranged in the stability zone of the solid solution, enough maintained to dissolve, partially or totally, the secondary phase grain size (carbides) in matrix (austenite) followed by the high speed cooling, to prevent the precipitation of the secondary phase and to maintain the solid solution in solved state, thus under-cooled and supersaturated.

After treatment a homogeneous austenite was gotten where the carbides of steel were dissolved.

- the second treatment is named sensitiveness and it consist of the heating between 650-680°C, with maintain at heat 1 – 2 hours for a massive precipitation of the carbides at grain size borders.

- thus treated the steel is corroded by boiling in an aqueous solution of 10% H_2SO_4 + 11% $CuSO_4$ for 48 hours. Steel becomes breakable, so that, after this operation, by mortaring, stainless steel fine powder is gotten.

In the engineering industry, in the hot-rolling departments, the surface laminates is covered with a layer of dross (oxide) to be removed by different methods work because the damage and harm the quality of equipment processed material. Skims layer consists of three types of oxides: FeO (wüstite), Fe_3O_4 (magnetite), Fe_2O_3 (hematite).

In cold rolling departments, the hot rolled band is cleansed of dross layer by chemical etching with acid solutions (HCl or H_2SO_4).

In the technology of the cold strip rolling, an important operation is the pickling of the semi-finish (hot rolled strip) to remove the oxides and to clean the strip surface.

A solution of H_2SO_4 is used, having the concentration of 15 – 20% in water at temperature of 80 - 90°C. The following chemical reaction take place:

$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O$

$Fe_3O_4 + 4H_2SO_4 = Fe_2(SO_4)_3 + FeSO_4 + 4H_2O$

$FeO + 4H_2SO_4 = FeSO_4 + H_2O$

$Fe + H_2SO_4 = FeSO_4 + H_2$

Also, in the bath, the reduction of the ferric salts to the ferrous salts takes place in the base of reaction:

$Fe_2(SO_4)_3 + H_2 = 2FeSO_4 + H_2SO_4$

After pickling, an important quantity of the crystalline light-green ferrous sulphate $FeSO_4 \cdot 7H_2O$ (vitriol iron sulphate) is gotten and, which is easy oxidated in contact with the oxygen of the air.

Ferrous sulfate is practically a waste resulting from the etching. It can be sold or used for industrial water treatment industry dyes, medicines, agriculture.

The crystallized ferrous sulphate $FeSO_4 \cdot 7H_2O$, and waste- water of the sulphuric acid pickling installation could be used, with good results, to get some aqueous or non-aqueous systems, which contains the iron oxides or hydrated oxides, in colloidal state or in suspension.

Finally it seeks magnetite (Fe3O4), a powder with good magnetic properties and different uses. A simple method for obtaining Elmore Fe3O4 was experienced since 1938 and consists of magnetite precipitation from solutions of salts of bi-and trivalent iron, by the action of excess sodium hydroxide.

This method was applied based on the solution of FeSO4 • 7H2O Etching bands resulting from the Cold strip mill at Mittal Steel Galati. It is usually added and a solution of FeCl3 • 6H2O.

This method used the chemical reaction:

$Fe_{(aq)}^{+2} + 2Fe_{(aq)}^{+3} + 4HO^{-} = Fe_3O_4 + 4H^{+}$

Fe_3O_4 is gotten in suspension or colloidal solution in various aqueous or non aqueous mediums.

In order not to cause a rapid decrease in pH - his alkaline solution is added in excess (10% NaOH in water).

After precipitation of Fe_3O_4 oxidation process can proceed both in solution and in the suspension during filtration, washing and milling.

Technology of getting Fe_3O_4 from solution, which contains Fe II and Fe III atoms from the system, the following operations are presented in figure 1.

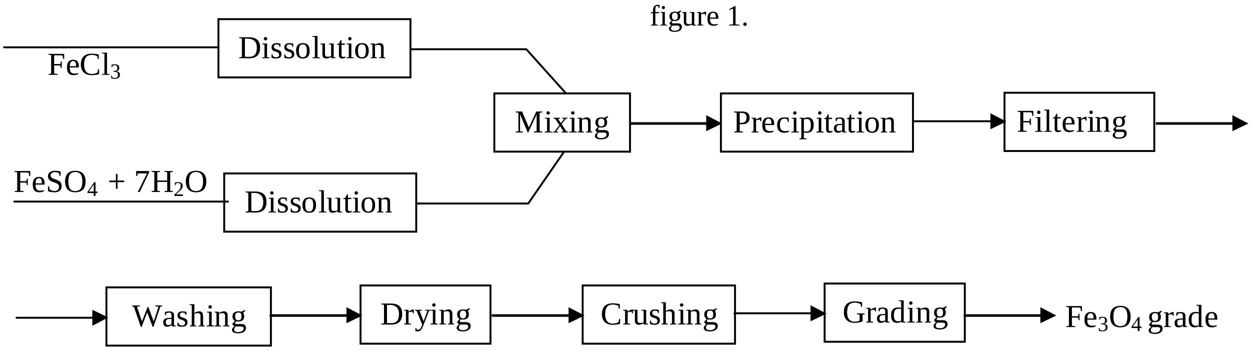


Figure 1 *The main operations of getting Fe_3O_4 from solution*

Dissolution is made in distilled water to prevent further oxidation and eliminate some of the physically dissolved oxygen.

The mixing done so that the oxygen of atmosphere is not driven in solution rather than in small extent.

The mixed oxides of Fe II and Fe III is known as magnetite (ferroferric oxides) in technic; it is spinel type ($M^{II}O \cdot H_2^{II}O_3$) with magnetical characteristics. The numerous utilizations it has, both as the colloidal state (magnetical fluid) and in the shape of the dried powder in electronic and electrical engineering, radio-broadcasting, non-distructive control and electro-domestic equipments. Filtering is made by the underpressure filters, maintaining a liquid cushion, as long as possible, on the precipitation surface. In the same way running and washing.

The drying is made in vacuum drying stove at 105°C to avoid oxygen action on the precipitate. Depending on how to exploit Fe_3O_4 obtained through this process, choose the appropriate size range. Sorting can be done on an assortment of vibrant site. If they need a very fine grained (<1 µ m) provides a wet or dry milling. An optimum grain can be obtained by passing an appropriate aqueous phase precipitated in the organic phase. Keeping quasicoloidale very fine particles in solutions can be achieved with surface-active systems. Oleic acid precipitate moisten and mix one more time, so that each particle to be covered with a thin film of oleic acid, which will prevent congestion. For an advanced mixing colloid mill can be used according to the method Bibik [..]

Finally you can add a quantity of toluene for a variable density, depending on the purpose. You get a ferrofluid with magnetic properties with multiple uses:

- ferrofluid seal;
- ferrofluid bearings;
- the effects of levitation applications;
- ferrofluid systems of writing and posting.

The powder obtained by precipitation method is black, very fine, the reason is not flowing, form small clusters and is magnetic. Density is about. 0.33 g/cm3. Particle size, d = max.3, 7 µm Diffractometer analysis showed a high purity of the powders (Fig. 2)

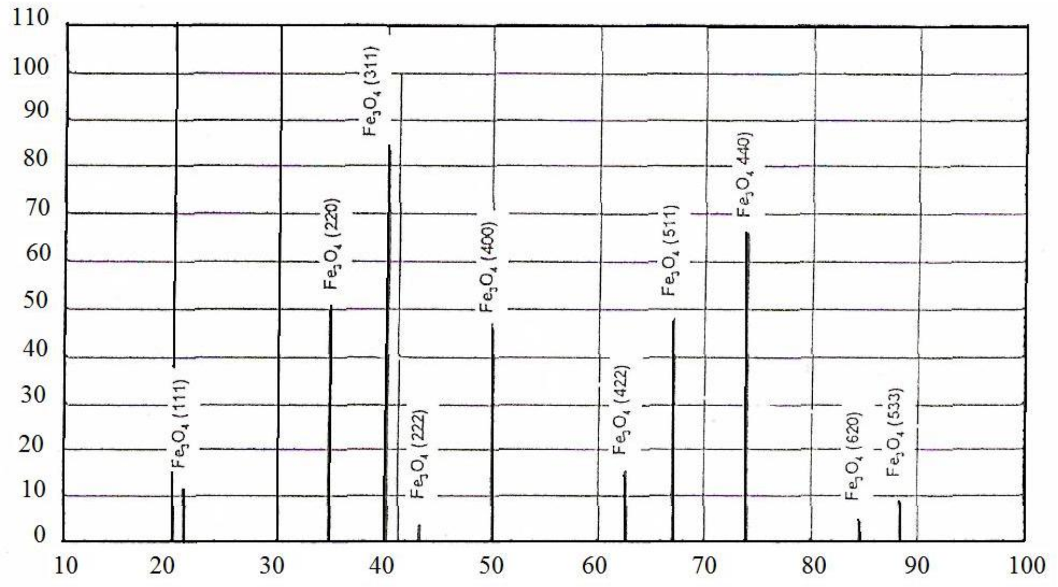


Figure 2 *Fe3O4 powder diffractometry*

2. Conclusions

To get high purity metallic powders from the metallic or non-metallic scraps is one of the up to date method of higher valorification of the scraps, from the metallurgical plants. Non-polluted “clean-technologies” are used, generally, with low consumption of energy and materials.

Technologies require simple installation with high performances

By a good management of the technological operation the wished purity of powder could be gotten, into a large range of grain size, grain shapes and with multiple utilisations.

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