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REDUCING THE ZINC EMISSIONS BY UPGRADING OF STEEL SCRAPS QUALITY

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ABSTRACT

The steel production is one of the major sources of heavy metals emissions to the environment. There are several possibilities for prevention and minimization of these pollutants. Emission reduction measures focus on add-on technologies and process modifications (including operating control). The prevention of the raw materials use that may have an unacceptable environmental impact in steel manufacture is important in achieving good environmental performance. A preventive measure specified by steel making BAT is the lowering the zinc-content of scraps. A way to make this possible is to treat these scraps before their charging in the furnace (BOF or EAF). In this paper a method for removing zinc surface layers of galvanized steel scraps is studied. The principle of separation is based on the difference in vapor pressures and stabilities with the formation of zinc and iron chlorides. A series of thermal experiments was carried out in an atmosphere of gaseous HCl. As result of the treatment applied on galvanized steel samples, zinc surface layers were removed and steel scraps remain unattacked.

KEYWORDS: zinc emission, steelmaking process, galvanized scrap cleaning, chlorination

1. Introduction

In the conventional integrated steel manufacturing process, the ferrous scraps along with iron from the blast furnace in molten form are converted to steel in a basic oxygen furnace (BOF).

Also the scraps form the metallic feedstock for obtaining the steels in an electric arc furnace (EAF).

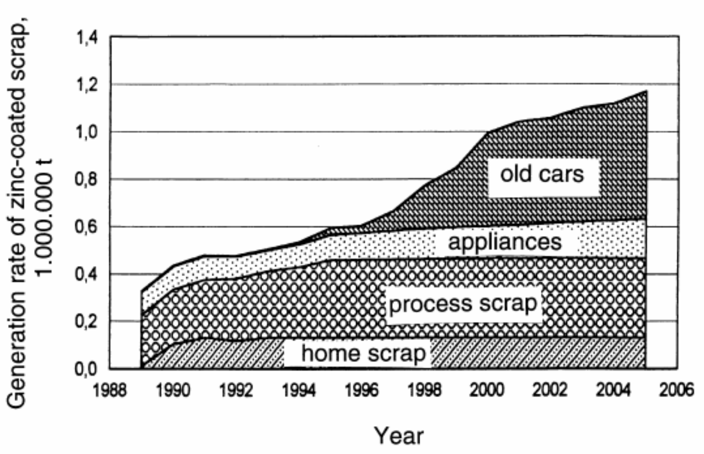


Fig. 1. *Development of the generation rate of scrap from zinc-coated steel in Germany*

This feedstock for steel manufacturing encompass a variety of different steel scraps and qualities derived from three categories: home scrap arising during steel making, process scrap from steel use and obsolete scrap at the end of the products' lifetime. Many of obsolete scraps are contaminated with galvanized coatings. In accordance with continued development of the production of zinc-coated steel the quantity of obsolete scrap originating from zinc-coated steel has registered a permanent increasing in the past years, Figure 1 [1 - 3].

The coating weight of these protective layers (Figure 2) varies from 40g/m^2/2-sides for coating weight obtained on electrogalvanized steel sheet to 610g/m^2/2-sides for coating weight deposed by hot dip galvanized process [4].

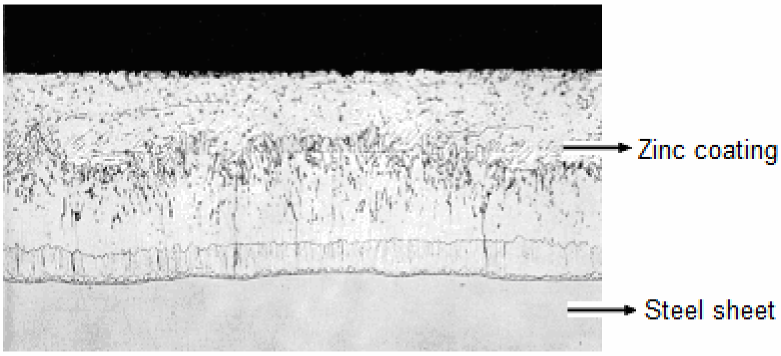


Fig. 2. *Cross section of galvanizing coating at surface of the steel sheets*

In terms of environmental the presence of zinc in steel scraps is undesirable, because more important part of this will eliminate as pollutant from steel making processes.

Large amounts of galvanized steel are produced world-wide, which will lead to the generation of dusts/sludges with a relatively high Zn content when the steel will become available as scrap in the steelmaking process. Moreover dust emissions contain higher levels of zinc and other heavy metals contained in the zinc coating. As result the steel production is a major source of zinc emissions. When galvanized scrap is melted in a steelmaking furnace, the zinc is volatizes and emitted as Zn oxide mainly airborne in the flue gas. At most BOF zinc is mainly emitted from the converter in the first few minutes of oxygen blowing.

All zinc emitted is transferred to air emissions from steel manufacturing using the BOF may include PM (ranging from less than 15kg/t to 30kg/t of steel). The stricter regulations about environmentally protection require flue gas treatment. Several methods (dry or/and wet) already used to clean up the environment from this kind of contaminant [5]. Most of them are costly.

The costs of the recycling technologies for the resulting zinc-laden dust and sludge by-products are also significant. Increased levels of zinc in the BOF dust make its usual recycling route via the sinter plant/blast furnace problematic because of the harmful effects of zinc in the blast furnace. By other hand at cleaning methods application is difficult to get optimum results. Thus its emission to air remains significant: as particulate matter and also as fumes produced for example during charging, tapping and casting. Zinc emission to water from wet dedusting process must be considered. Wastewaters generated from steel manufacturing using the BOF include 14 mg/L zinc. This BOF scrubber discharge water usually requires treatment to lower its zinc content. As a consequence of the major problems associated of this pollutant and its persistence in contaminated soil when it is finally deposed (contamination of soil appears to be virtually permanent because the first half-life of zinc, for soils in lysimetric conditions, varies greatly between 70 to 510 years [6]), the zinc emissions must be perpetually monitored. For BOFs integrated into iron and steel manufacturing plants, specific emission value for zinc is 8.2 g/t liquid steel. The target of zinc emission level per metric ton of product is 3g. Also maximum value for zinc emission into effluents from iron and steel manufacturing plants must be 2 milligrams per liter. According to recommendations PARCOM-ATMOS, the zinc emission level in the dust emitted at melting for EAF process is in the range 20-90g/t [7]. BATs on the Production of Iron and Steel Associated Emission levels recommend the following values for zinc [8]:

- BAT Associated Emission Levels for Emissions to Air

  - Emission Level of zinc = 5 - 10 mg/m^3

- BAT Associated Emission Limits for Discharges to Water

  - Emission Level of zinc = 0.5mg/L unless otherwise stated.

To prevent and minimize the presence of zinc and other heavy metals from the surface of the protected steel scraps, must to implement the operating practices e.g. to remove zinc-bearing components prior to recycling in secondary steel facilities.

The lowering of the zinc-content of scrap is distinguished as process-integrated measure recommended among the techniques considered in the determination of BAT for the steel industry. Techniques to consider in the determination of BAT In the literature there are several methods described to remove coatings from the surface of scrap that are efficient to zinc recycling. These can be divided into two main principles: leaching and thermal treatment. Research regarding leaching based on acid solutions (HCl, H_2SO_4) and basic solutions (NaOH) are covered in the literature [9]. In 1987, Argonne and its industrial partner, Metal Recovery Industries, U.S., Inc., sought to develop a new technology for converting galvanized scrap to clean scrap for steel making. The zinc is dissolved in a hot-water solution (70 to 90°C) of about 20 to 32% sodium hydroxide [10]. The metal chlorides formed by gaseous HCl released by the pyrolysis of PVC to remove surface layers from plated materials were proposed [2, 11-14] have been concentrated on the possibility to vaporize coatings with an air and chlorine gas mixture. Chlorination method was studied for recycling galvanized steel scrap. In this paper a method for removing zinc surface layer from the surface of the galvanized steel scraps is studied. The principle of separation is based on the difference in vapor pressures and stabilities with the formation of zinc and iron chlorides. A series of thermal experiments was carried out in an atmosphere of gaseous HCl.

As result of the treatment applied on galvanized steel samples, zinc surface layer was removed and steel scrap was remaining unattached. The economic removal and recovery of the zinc coating from scrap prior to melting would provide a number of cost and especially environmental advantages. The recovery of the zinc from the chemical solution is easily. Air and chlorine are readily available, and volatile chlorides are easy to separate

2. Experimental and materials

Experiments were carried out in a precinct which was placed in a chamber furnace, Figure 3. Air with gaseous HCl was mixed to obtain an atmosphere that was constantly maintained and utilized for obtaining an acceptable rate of removal. In accordance with literature an O_2:Cl_2 molar ratio of 10:1 is used [13, 15].

The literature specified that in these conditions the metal losses are acceptable and the chlorine is selectively reacting with the zinc.

Heat treatments were conducted at variable temperatures from 570 to 860^{0}C to establish the optimum thermal regime. Each sample was maintained then minutes to a constant temperature preheating and then it was slowly cooled in the air.

For the zinc-plated steel samples the electrolytic galvanized sheet scraps from car body were used.

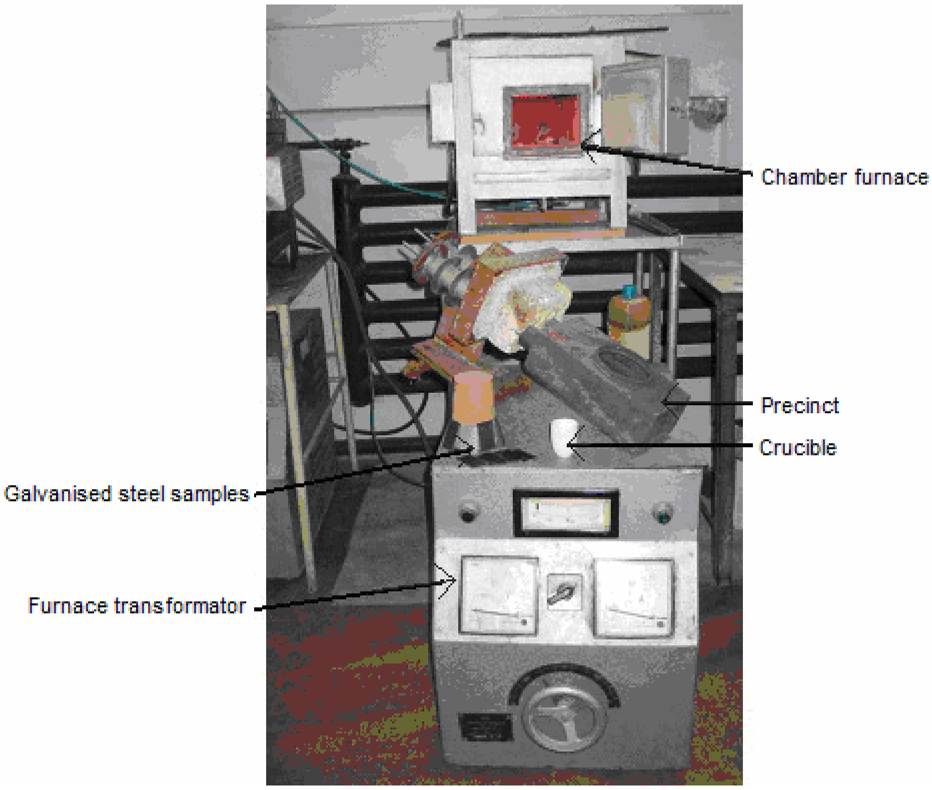


***Fig. 3.** Experimental installation for the galvanized steel scraps treatment*

3. Results and discussions

Each test used hydrochloric acid as the chlorine source. The removal of the zinc coating is based on its evaporating in this gas phase. The optimum process parameters were established by analyzing the vapors pressures of chlorides of metals (Figure 4).

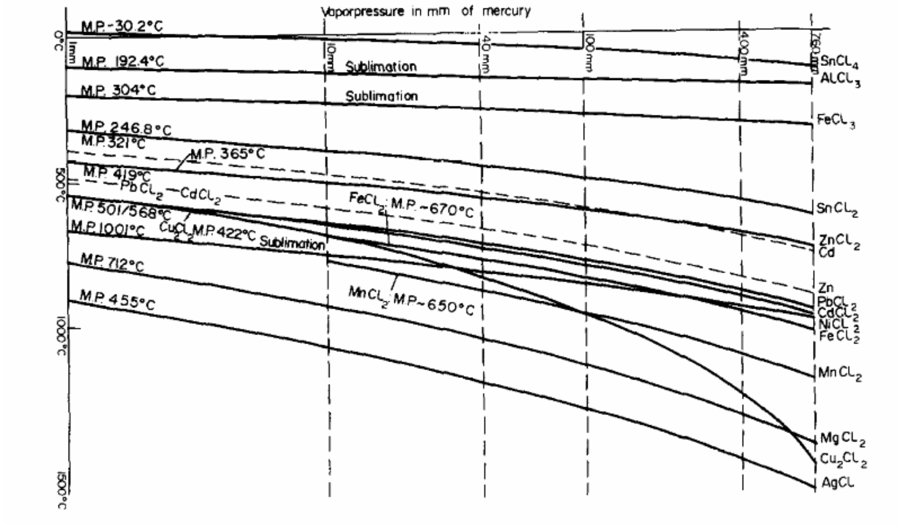


Fig. 4. *Vapors pressures of chlorides for some relevant metals [16]*

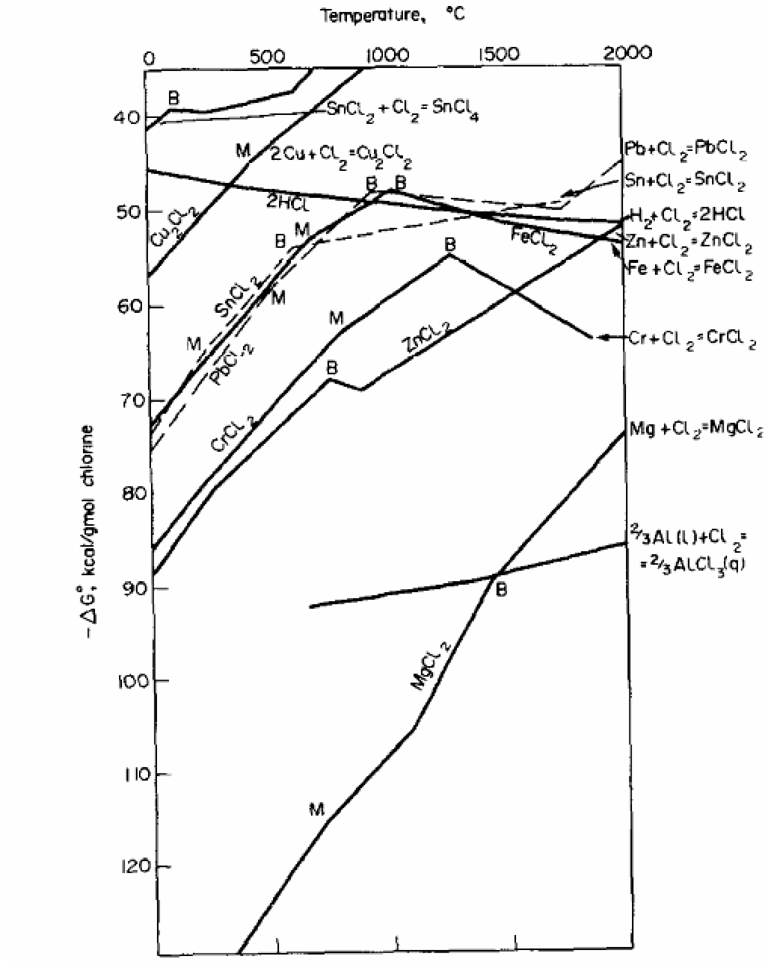


Fig. 5. *Standard free energies of formation for metal chlorides [16]*

Also has been taken into account the standard free energies of the metals chlorides formation as functions of the temperature (Figure 5). The possible reactions together with their respective standard free energy changes (ΔG^0) are given in the following equations (Table 1).

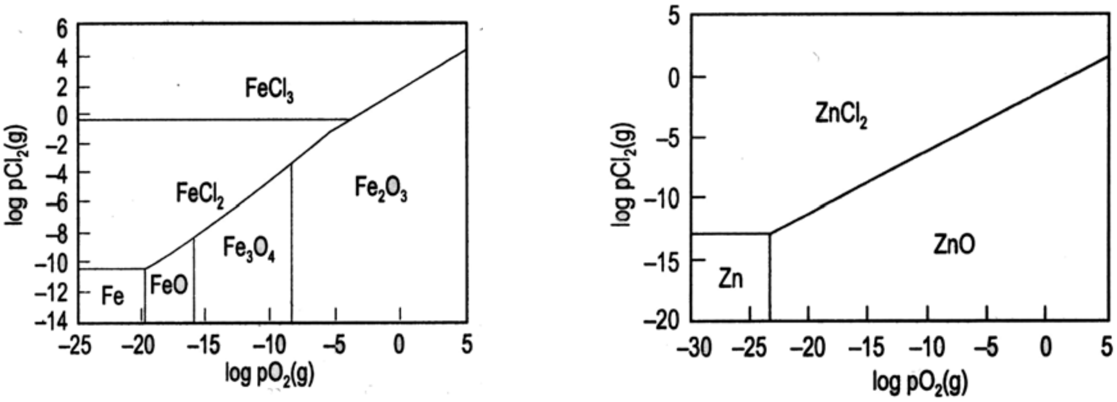
***Table 1.** Standard free energy changes, ΔG^0 [18]*

Reactions	**ΔG^0,** kJ/mol (at 800 ^{0}C)
$Zn(l) + Cl_2(g) \rightarrow ZnCl_2(g)$	- 272.430
$Zn(l) + 1/2\ O_2(g) \rightarrow ZnO$	- 240.160
$ZnO + Cl_2(g) \rightarrow ZnCl_2(g) + 1/2\ O_2(g)$	- 32.270
$Fe + 1/2\ O_2(g) \rightarrow FeO$	- 202.347
$3\ FeO + 1/2\ O_2(g) \rightarrow Fe_3O_4$	- 163.111
$2\ Fe_3O_4 + 1/2\ O_2(g) \rightarrow 3\ Fe_2O_3$	- 86.371
$Fe_3O_4 + 9/2\ Cl_2(g) \rightarrow 3\ FeCl_3(g) + 2\ O_2(g)$	+ 73.550
$Fe_2O_3 + 3\ Cl_2(g) \rightarrow 2\ FeCl_3(g) + 3/2\ O_2(g)$	+ 77.831

The zinc removal is greatly dependent on the gas composition and temperature.

The thermodynamically data show that under reducing conditions only volatile zinc is thermodynamically stable, whereas under oxidizing conditions solid ZnO and volatile $ZnCl_2$ are present in about equivalent amounts. Up to a temperature of about 1900 ^{0}C, $ZnCl_2$ is more stable than $FeCl_2$. Moreover $ZnCl_2$ is more volatile than $FeCl_2$.

Up to temperatures of about 670 ^{0}C, the vapors pressure of $FeCl_2$ is almost zero. Formation of $FeCl_2$ will be suppressed as long as metallic zinc is present. The phase stability diagram (Figure 6) shows that with an O_2:Cl_2 ratio of 10:1, zinc exists as $ZnCl_2$ and iron as hematite, Fe_2O_3 [15].



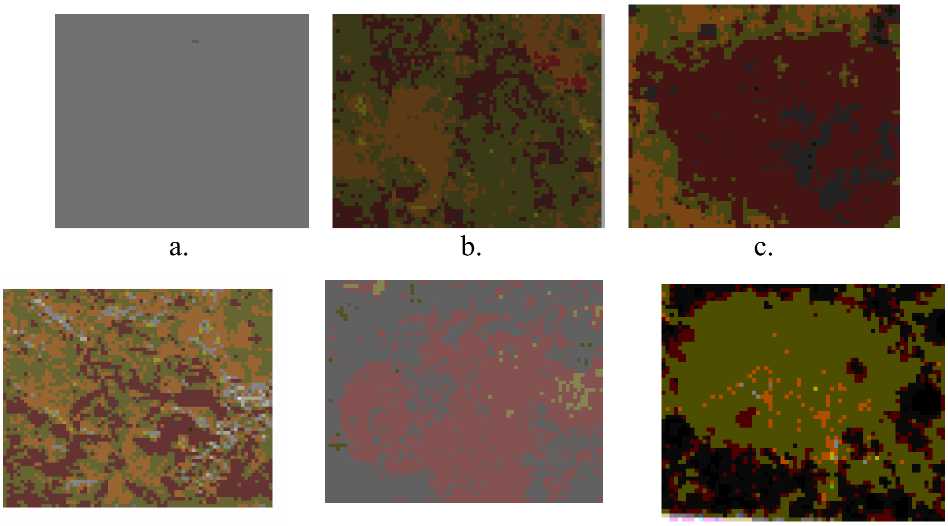
a b

***Fig. 6.** Phase stability diagrams for the systems Fe-O_2-Cl_2 (a) and Zn-O_2-Cl_2 (b) [13]*

During chlorination at the varied heating temperatures, the appearance of the galvanized steel samples is modified. Their aspects are dependent which on the gas composition also. Theirs comparable evolution is given in Figure 7.

A lower temperature the zinc removal rate is significantly reduced.

The high zinc removal efficiency as result of fast reaction was developed at high temperature (up to 700ºC): at 570^{0}C, small areas of the unconsumed zinc coating (grey areas) and zinc free-zone composed by the ferric oxide (red areas) are present (Figure 7b); ferric oxide is greatly extended of the all area (homogeneous red areas) at 680^{0}C and small oxide areas are detached from the surface sample (Figure 7c); at 790^{0}C and decreasing of the chlorination conditions ferric oxide areas (red color) alternate with ferroferric oxide areas (black color) appear (Figure 7d); at 860^{0}C, Fe_2O_3 are predominantly (Figure 7e).


a. b. c.

c. d. e.

Fig. 7. *Aspect of samples after chlorination at different heating temperatures: initial steel sample before its heating (a); 570 ^{0}C (b); 680 ^{0}C (c); 790 ^{0}C (d); 860 ^{0}C (e)*

The microstructural analyses of selected samples reveal the removal of zinc coating at preheating of steel samples into chlorine atmosphere, Figures 8-10. The selected samples were those from 570, 680 and 860^{0}C.

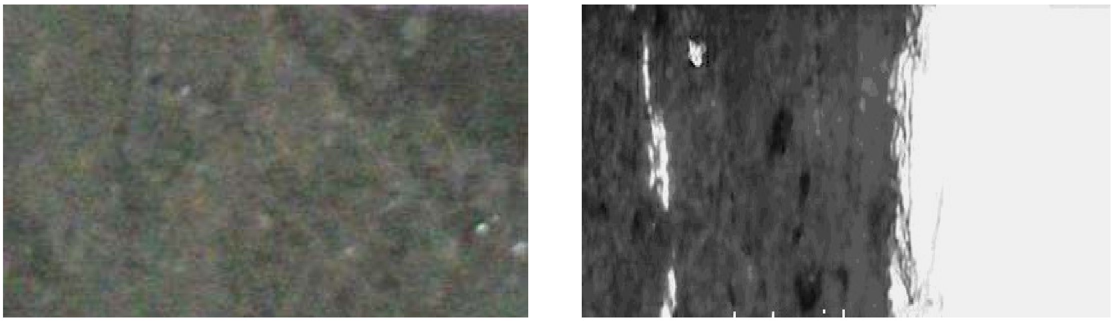

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Fig. 8. *Surface of the zinc coated steel scrap after treatment (temperature 570^{0}C) (a) and microstructure of the sample (500x) (b)*

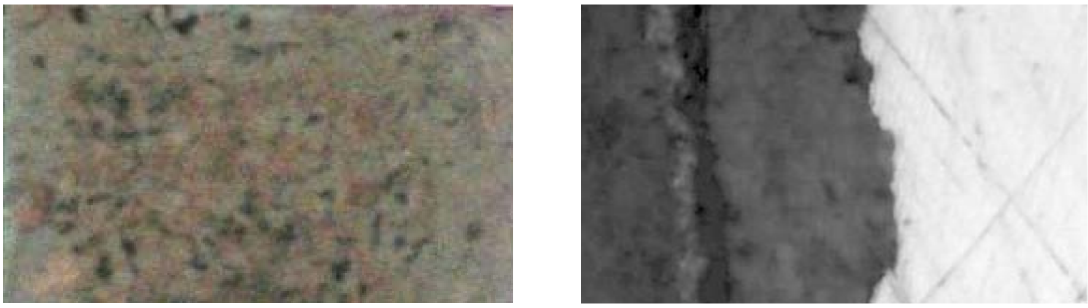
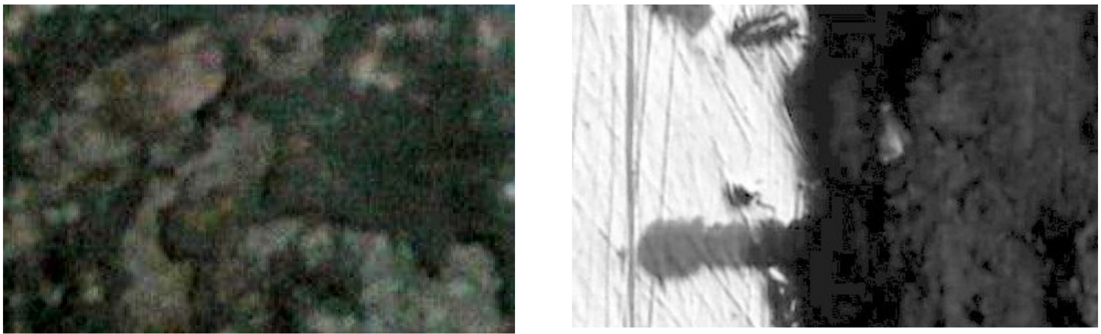

a *b*

Fig. 9. *Surface of the zinc coated steel scrap after treatment (temperature 680^{0}C) (a) and microstructure of the sample (500x) (b)*



a *b*

Fig. 10. *Surface of the zinc coated steel scrap after treatment (temperature 860 ^{0}C) (a) and microstructure of the sample (500x) (b)*

For the treatment at temperature up to 800 ^{0}C, the structural analyze put in evidence a strongly oxidized zone with intergrains attack (about 5 - 6μm depth). The steel is corroded and the iron oxides Fe_2O_3 and Fe_3O_4 are formed (thickness of this layer is about 12 - 13μm). In this case the quality of the steel scrap is affected by oxidizing process of iron.

4. Conclusions

The removal of the zinc as contaminant from steel scrap leads to upgrading the steel scrap quality. The quantity of the Zn-containing dust and arising in the flue gas produced at steel making process is reduced. That led to diminishing of the cost for the dedusting operation and to lower zinc emission to air. Also the zinc emission from waste water released from wet dedusting installation.

Chlorine has been shown to be an effective reagent to remove zinc as $ZnCl_2$. As result of the treatment applied on galvanized steel samples, zinc surface layers were removed and steel scraps remain unattacked. The zinc removal has been as high as 99% at preheating temperatures ~ 700ºC. Over this temperature, the quality of the steel scrap is negatively influenced. The higher temperature and the increasing of the O_2:Cl_2 ratios are favorable for developing the interaction between iron and oxygen. The formation of the scale is passed in the depth of the heated steel. Must be specified that one grade of galvanized steel were used in all experimental tests. For industrial conditions the chlorination process must be adapted to different steel qualities with variable compositional layers.

In the industrial steel making plants, the energy contained in the flue gas emitted from furnaces (BOF or EAF) can be valorized. By this way the energy consumption is reduced.

The conditions for dioxins forming must be taken in account. The selection of the steel scrap must be accurately carried. The advanced eliminating of other contaminants that are mixed with the metallic feedstock is necessary. At steel scrap preheating the presence of certain metals is favorable for the dioxins formation (by „novo synthesis process"). Copper, iron, zinc, aluminum, chromium, and manganese are known to catalyze PCDD/PCDF formation [18].

The formation of the chlorides involves an important risk associated to corrosion of the process equipment. For this reason these must be collected and decomposited for chlorine recovery.

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