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Recycling Technology of Waste Product in Electro Galvanizing Line of Steel Company

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This technology provides an economical production of high value added goods applicable to electro chemicals by recycling of waste products in EGL(Electro Galvanizing Line). The waste products produced in EGL contain potassium chloride (KCl), nickel and zinc. Highly pure KCl and Zinc Chloride which are raw material of electro plating, can be produced by the development of the recycling process. The scope of this study ranges from laboratory experiments to pilot test in plant. We have developed the whole process of recycling technology such as purification method of waste products, fabrication methods of electro chemicals, basic design of plant, pilot scale production and evaluation of pilot goods. Developed electro chemicals were pure enough to satisfy the specification of steel company.

Keywords: EGL, potassium chloride, Zinc chloride, Waste, Recycling.

Introduction

In an electro galvanizing line(EGL) of a steel manufacturing company, a cold rolled steel sheet is electroplated for automobiles by using an electrolyte containing Zn or Ni ions. The waste products like spent electrolyte are produced in the process of electroplating inevitably. The waste products produced in EGL has threatened the safety of plant, but they contain high concentrated potassium chloride (KCl), nickel and zinc ions, which can be economically recyclable. [1]

Chemicals such as potassium chloride and zinc chloride are raw material of electroplating, which is imported from other country. These chemicals demand high purity (>99.5%). Generally, electro chemicals are manufactured by complicated process of removing the impurities [1,2]. The grade of chemicals is classified with their purity. However, in order to manufacture high purity electro chemicals, high purity raw material has to be used and a complicated purification process has to be performed, which result in high manufacturing cost [3,4].

However these chemicals can be produced from the waste products of EGL by the development of suitable recycling process. The most important technologies in the fabrication of electro chemicals are the purification of waste products and separation of valuable composition from waste material. [5] We have investigated on the various purification processes in this study and tried to find an economic process of recycling.

The Summary of Recycling Process

The laboratory-scale experiments, the pilot experiment, the design of plant, the production of pilot goods and the test of pilot goods were carried out. First of all, the authors have tried to develop the purification process and basic recycling process of wastes.

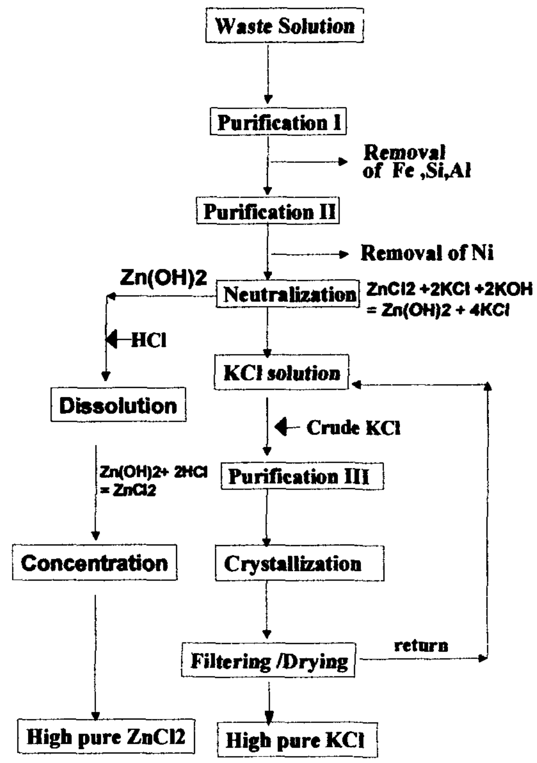

Figure 1 The recycling process of electro chemicals by waste solution of electro galvanizing line.

Figure 1 shows the flow diagram of the fabrication of electro chemicals. The waste solution has to be purified to meet the electro chemicals. Fe ,Si, Al can be removed by the oxidation/precipitation process (purification I). [6] The Ni ions should be removed by cementation method (purification II) to fabricate the electro chemicals like $ZnCl_2$ and KCl.

After the main impurities are removed, the potassium hydroxide is added into the purified solution. The chemical reaction is as follows;

$ZnCl_2 + 2KCl + 2KOH = Zn(OH)_2 + 4KCl$ (1)

Zinc ions are precipitated as hydroxide. White suspensions of zinc hydroxide are filleted. The solid cake (zinc hydroxide) is dissolved in high concentrated hydrochloric acid to fabricate the zinc chloride solutions for electro chemicals.

The filtered solution contains high concentrated KCl. As known in reaction equation (1), KCl in waste solution increases with neutralization. The crude KCl used as an agriculture raw material which is much cheaper than electro chemicals is added to enhance the concentration of KCl in solutions. Then the purification process is followed to remove the impurities coming from crude KCl. The pure KCl solutions are heated and saturated by an evaporator to form a crystallized potassium chloride.

The Results and discussion

Purification of impurities

The concentration of recyclable elements and impurities of general waste solution are displayed in table1. KCl and Zn are recyclable element, however Ni, Fe, Pb, Cu are impurities which should be removed. Some of spent electrolyte contains high concentration of impurities like Fe, Si and Ni. Fe and Si ions come from the steel strip, the anode and the sludge filter. Ni ions are originated from Zn-Ni electrolyte itself.

Table 1 The composition of waste Zn and Zn-Ni electrolyte produced in electro galvanizing line.

Electrolyte	resource (g/l)		Impurities (ppm)			
	KCl	Zn	Fe	Ni	Cu	Si
Zn	570	95	10	4	3	5
Zn-Ni	590	97	900	1300	5	700

As seen in figure 1, three different process of purification are investigated. The first process of purification (purification I) is the oxidation / precipitation process to remove Fe ,Si, and Al. The waste solutions are oxidized to precipitate Fe ions as a sludge like $Fe(OH)_3$ or FeOOH. If the formed sludge were filtered, Fe ions can be removed from solutions.

The pH of solution was controlled by potassium hydroxide. The waste solution is bubbled with air. The hydrogen peroxide is added in the waste solution to transform the ferrous ion to ferric ions. Ferric ions have low solubility in water at high pH of solution. Thus Fe can be removed by oxidation and precipitation process. [6]

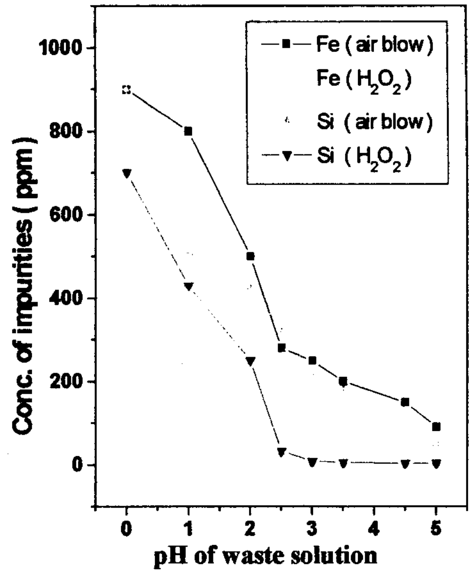

Figure 2 The concentration of impurities with oxidation condition and pH of solution.

As presented in figure 2, the concentration of Fe and Si ions varied with oxidation condition and pH of solutions. As the pH increases, the concentration Fe and Si decreases. The hydrogen peroxide as an oxidizing agent is more effective than the air. When pH of solutions over 2.5, Fe and Si ions can be removed up to 3 ppm. Si ions was found be removed simultaneously with the precipitation of Fe sludge. Generally Fe sludges adsorb the Si sludge because the electric charge of sludge is different from each other.

The second process of purification (purification II) used in this study is electro chemical reaction called as a cementation process. Noble ions like Ni, Pb, Cu ions can be precipitated by adding Zn powder into solution. Especially the optimum conditions to remove Ni ions were investigated in this study. Figure 3 shows the Ni removal effect with various conditions.

Zinc powders with two different sizes are used in this study (ZD20: 20μm , ZD12:12 μm). Adding amount of zinc powders is 26 and 13 g/liter, which is equivalent to Ni concentration of solution. Reaction temperatures are 25°C and 60 °C respectively. After zinc powders are added, mixing during reaction time and filtering are followed. Ni ions decreased with reaction time. The higher temperature and higher adding amounts are more effective. ZD 12 with fine size can reduce the reaction time of reaction.

The third process of purification (purification III) used in this study is the oxidation / precipitation process to remove Fe which comes from crude KCl. The crystallization process to fabricate solid KCl can play an important role on removal of impurity like Na and Ca.[7]

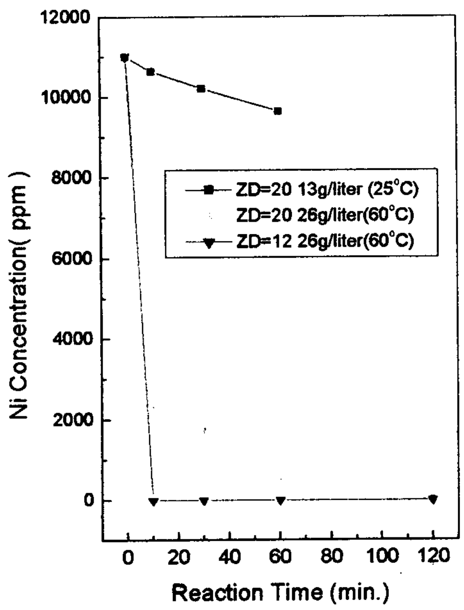

Figure 3 The concentration of Ni with various reaction conditions

Fabrication of potassium chloride

There are two important technologies to fabricate potassium chloride of good quality. One is impurity removal to be pure and the other is the control of size and shape of KCl.

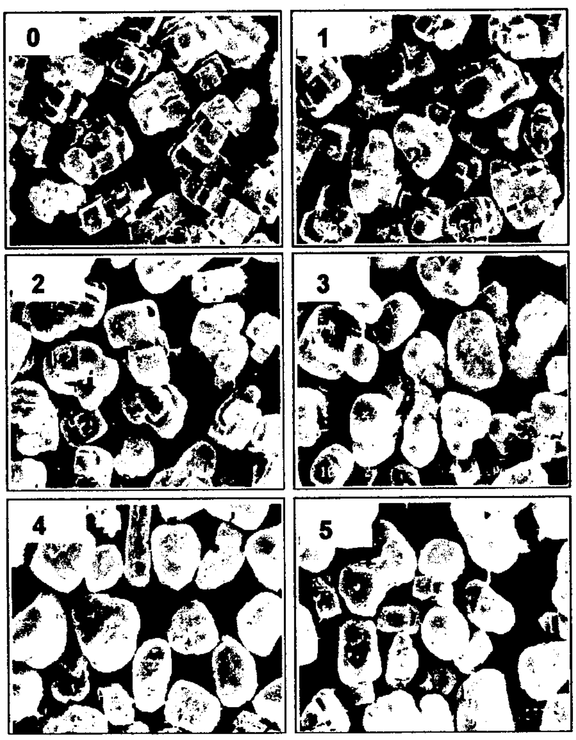

Figure 4 The shape and size of KCl with crystallization time (the number remarks the hours of mixing).

Potassium chloride has a property that absorbs water and results in caking. Caking means the hardening of KCl, which is not easy to handle. The shape and size should be controlled to prevent caking of KCl. As shown in figure 4, the shape and size of KCl has been changed with mixing time. As the increase of mixing time, potassium chloride grows from rectangular to sphere. Well-fabricated spherical KCl has an anti-caking property.

Fabrication of zinc chloride

After removing Ni ions in solution, neutralization with potassium hydroxide is followed. Figure 5 shows the variation of pH with adding amounts of alkali. Zinc chloride forms two different hydroxide phases with pH of solutions. One is $ZnCl_2.4Zn(OH)_2$ and the other is $Zn(OH)_2$.

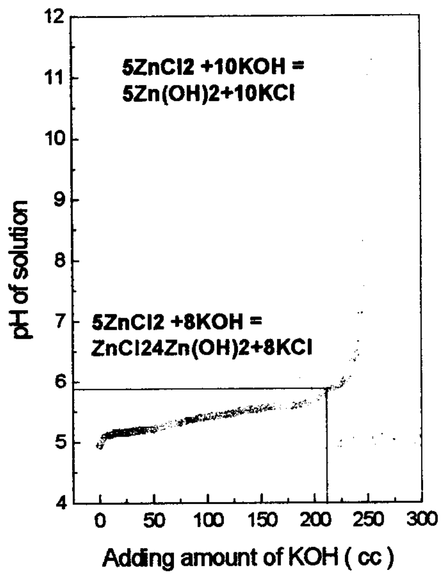

Figure 4 The shape and size of KCl with crystallization time.

Zinc hydroxides were dissolved in high concentration of hydrochloric acid to make zinc chloride. The chemical reactions are as follows;

$ZnCl_2.4Zn(OH)_2 + 8HCl = 5\ ZnCl_2 + 8H_2O$ (2)
$Zn(OH)_2 + 2\ HCl = ZnCl_2 + 2H_2O$ (3)

As known in equation (2) and (3), the concentration of $ZnCl_2$ made from $ZnCl_2.4Zn(OH)_2$ is higher than that of $Zn(OH)_2$. Zinc chloride for electro chemicals is demanded for the high concentration of $ZnCl_2$(>62.5%). Thus heating and concentration step should be followed.

The concentration of $ZnCl_2$ can be monitored by specific gravity. The authors have tried to find a correlation between the concentration and density of $ZnCl_2$. Figure 5 shows the results of measuring the density with the concentration of $ZnCl_2$.

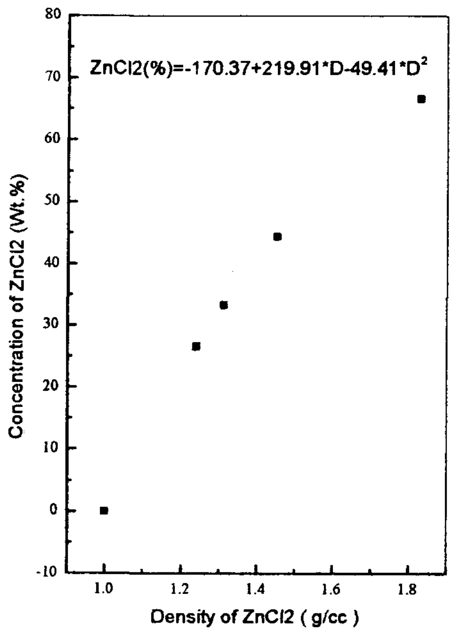

Figure 6 The correlation between the concentration and density of $ZnCl_2$

Evaluation of pilot goods

Pilot goods produced in the plant in figure 6 are tested for suitability of electro chemicals. Table 2 and 3 show the results of chemical analysis of developed potassium chloride and zinc chloride. Impurities of electro chemicals act as sludge former and have a detrimental effect on the microstructure and productivity of electroplated steel. Thus the electro chemicals are demanded for high purity. The developed goods meet the specification of electro chemicals of steel company.

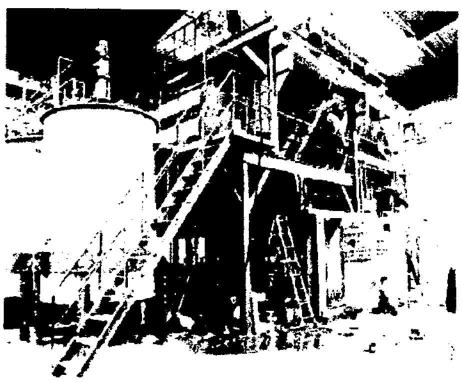

Figure 6 Recycling plant for the fabrication of electro chemicals by the waste in EGL

Table 2 The comparison of chemical analysis of KCl between the specification and the developed.

	Concentration	Impurities (ppm)			
	(Wt%)	Ca+Mg	Fe	Cr	Cu
Specification	>99.5	<350	<5	<1	<5
Developed	>99.5	17	0.1	Tr.	0.5

Table 3 The comparison of chemical analysis of $ZnCl_2$ between the specification and the developed.

	Concentration	Impurities (ppm)			
	(Wt%)	Fe	Cr	Cu	Pb
Specification	>62.5	<10	1	1	5
Developed	65.5	0.54	0.1	Tr.	Tr.

The developed electro chemicals were examined in a Zn-Ni electroplating test. The electro chemicals currently used in the factory were tested as a reference. From various electroplating test conditions, the results from the evaluation of electroplating are displayed in Table 4. We have evaluated the important properties of electroplating such as are brightness, whiteness, Ni content of electroplated steel sheet. Many specimens are made with electroplating condition like current density and temperature.

Table 4 The results of electroplating test for the developed electro chemicals.

	Whiteness	Brightness	Ni content
Developed	65-70	50-59	12.1-12.8
References	66-69	53-57	12.2-12.8

The maximum whiteness and brightness of developed are slightly lower than those of conventional one. However the minimum whiteness and brightness of developed is slightly higher than that of conventional one. As a hole the properties of developed potassium chloride are similar to the conventional high-grade KCl. As seen in figure 7, the microstructure of developed KCl is also similar to the reference.

(a)

(b)

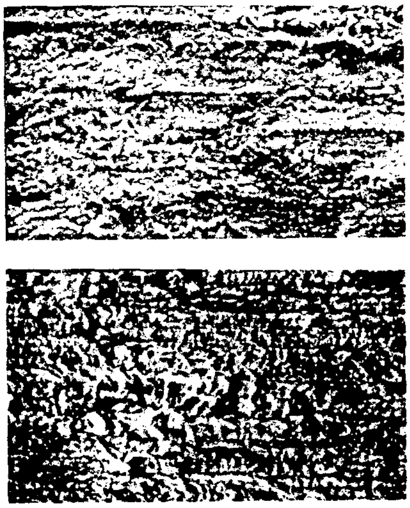

Figure 7 Comparison of microstructures of electroplated layer fabricated with different chemicals ((a): developed, (b): reference)

Conclusion

We have developed the whole process of recycling technology of wastes in EGL such as purification method of waste products, fabrication methods of electro chemicals, pilot scale production and evaluation of pilot goods. The results of this study are summarized as follows;

1. Impurities of Fe,Si can be removed by oxidation and precipitation process. As the pH increases, the concentration Fe and Si decreases. The hydrogen peroxide acts as effective agent.

2. The higher temperature and higher adding amounts are more effective. ZD 12 with fine size can reduce the reaction time of reaction.

3. Anitcaking KCl can be fabricated with the control of mixing time. The developed KCl can meet the specification of ..e use in steel company.

4. ZnCl2 developed in this study can meet the specification of POSCO in concentration and purity.

5. The developed electro chemicals were examined in a Zn-Ni electroplating test. The properties of developed potassium chloride are similar to the conventional high-grade KCl.

References

[1] J.Y.Lee , J.G.Sohn, H.H. Lee ; RIST Journal of R&D, vol.12,No2, 1998, P 184

[2] J.Y.Lee , J.G.Sohn, H.H. Lee ; RIST Journal of R&D, vol.8,No3, *1998, P 458*

[3] Dutrizac, T.E and Mac., R.J.C , Percolation Leaching of Petrandite Ore, *CIM Bull.*, Vol.67[743] 1974, P 169

[4] W. Betterige , *Nickel and It's Alloy*, John Willey & Sons, New York, 1984, P 22

[5] Jae-Young Lee et al, International Patent , PCT/KR94/00082, 1994

[6] E. Jackson, *Hydrometallurgical Extraction & Reclamation*, John Willey & sons, New York 1986, P 141

[7] Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, National Association of Corrosion Engineers, Huston, 1974, P 311