# CHAPTER II

# LITERATURE REVIEWS

## 2.1 Hydrometallurgical zinc production and waste from production

The hydrometallurgical process is the most common process to produce zinc from zinc ore. The hydrometallurgical zinc process consists of four steps: (1) roasting of zinc waste concentration, (2) leaching of zinc oxide, (3) purification of the leaching liquor and (4) electrowinning of zinc [7] as shown in Fig 2.1

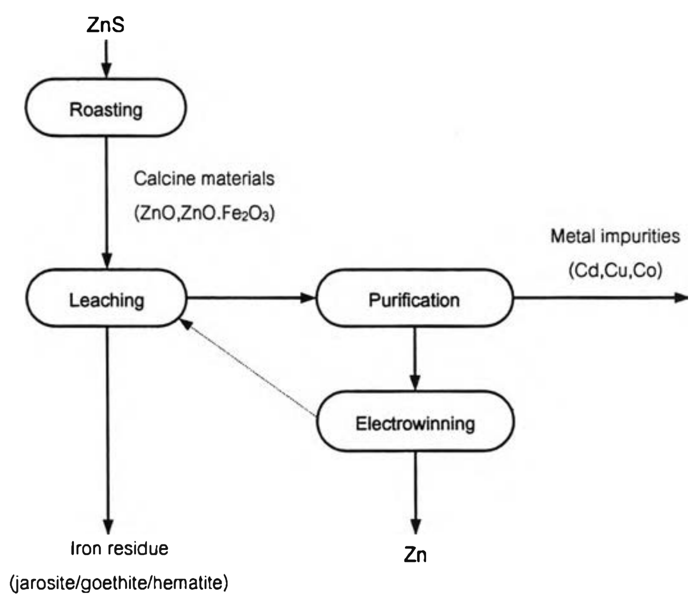


Fig 2.1 Hydrometallurgical zinc production process

Concentrated zinc sulfide (sphalerite (ZnS)) is roasted to produce mainly ZnO and also some zinc ferrite ($ZnO.Fe_2O_3$). Zinc ferrite was dissolved by hot $H_2SO_4$. Iron is subsequently precipitated from this solution as jarosite ($M^*Fe_3(SO_4)_2(OH)_6$), goethite (FeOOH) or hematite ($Fe_2O_3$). This precipitate also removes many metallic impurities. Other metal impurities such as cadmium, copper and cobalt are precipitated

* M = $K^+$, $NH_4^+$,$H^+$, Ag, 1/2$Pb^{2+}$ and $H_3O^+$

by cementation with zinc powder before electrowinning [2,7,8,9].

The main compositions of iron residue: jarosite, goethite and hematite from leaching process are shown in Table 2.1.

Table2.1 Chemical composition of jarosite , goethite and hematite [2].

| Iron residue | Composition | | |
|---|---|---|---|
| | Fe | Zn | S |
| Jarosite | 25-30 | 4-6 | 10-12 |
| Goethite | 40-45 | 5-10 | 2.5-5 |
| Hematite | 50-60 | 0.5-1 | 2-3 |

## 2.2 Quality control and standards of tiles

The general classification of tiles according to their application is mosaic tiles, wall tiles or floor tiles. The properties of these are described by DIN standard [10] as follow:

### 2.2.1 Mosaic tiles

Physical quality control and standard of mosaic tiles are observed:

- Water absorption less than 1%
- Dimension deviation ± 2%
- Thickness deviation ± 10%
- Rectangular deviation not exceed 1.0%
- Flatness of surface: centre curvature, edge curvature and warpage of the surface not to exceed 0.5%
- Bending strength: more than 12 $Kg/cm^2$.
- Resistance of glaze to acids and alkalis

### 2.2.2 Wall and floor tiles

Wall and floor tiles are conformed to the DIN standard as follows in Table 2.2.

Table 2.2 Physical quality control and standard of wall and floor tiles

| Requirements | Glazed floor tile | Unglazed floor tile | Wall tile |
|---|---|---|---|
| Length tolerance | ± 0.5% | ± 0.5% | ± 0.5% |
| Width tolerance | ± 0.5% | ± 0.5% | ± 0.5% |
| Thickness tolerance | ±5% | ±5% | ±5% |
| Straightness of edges | 0.5% deviation | 0.5% deviation | 0.5% deviation |
| Rectangularity of corners | 0.5% deviation | 0.5% deviation | 0.5% deviation |
| Evenness of surface (curvature) | 0.5% deviation | 0.5% deviation | 0.5% deviation |
| Surface appearance | No visible defects when examined at a distance of 1.0 meter from the tile surface under an illumination intensity of 300 lux | No visible defects when examined at a distance of 1.0 meter from the tile surface under an illumination intensity of 300 lux | No visible defects when examined at a distance of 1.0 meter from the tile surface under an illumination intensity of 300 lux |
| Water absorption | Max 8.0% | Max 5.0% | Max 18.0% |
| Flexural strength | Min 250 $Kg/cm^2$ | Min 250 $Kg/cm^2$ | Min 180 $Kg/cm^2$ |
| Scratch hardness of glaze | Min 5 Mohs | Min 6 Mohs | - |
| Thermal expansion 20 -100°C | Max $6.0x10^{-6}/^{o}C$ | Max $5.5x10^{-6}/^{o}C$ | Max $5.5x10^{-6}/^{o}C$ |
| Resistance to HCl solution (3% concentration) | pass | pass | pass |
| Resistance to KOH solution (3% concentration) | pass | pass | pass |

## 2.3 Ceramic stains

Ceramic stains, called pigments or ceramic colors have been made with combinations of no more than a dozen materials. These materials are silica, alumina, potassium, lithium, lead, zinc, boron, calcium, magnesium, barium and borax. They have been intermixed in a verity of ways.

Ceramic stains usually prepared by blending appropriate raw materials by dry mixing, wet milling or by preparing a slurry or slip from the powder from the powdered reagents. Wet milling is preferred. This requires to filtering and drying. After blending process, dry powders are calcined. The reasons for calcining the materials for ceramics stains are develop the color in an inert, stable formand to remove any gaseous compounds that may spoil the ware. The materials should be placed in a covered crucible of unglazed, bisque-fired porcelain or stoneware, which has been washed in a solution of one part flint, three parts water, to seal the pores. The materials are calcined at verity of temperature from cone 04 to 8 depend on the materials being used. The calcining process is critical as to temperature, time, draft, atmosphere and the crucibles. The calcining also must be closely controlled because they have an important influence on the final color. Calcined ceramic stain is controlled to small enough pieces via grinding process. After grinding, the blends must be washed by levigation (put the blend in water, let them settle, decant, stir, repeat) to remove any remaining soluble salt and to separate the fine grains from the coarse. When dry, they are ready for use. The factors are critical to the proper preparation of ceramic stain as follow [11,12]:

1. Raw material: its type, quality, purity, density and uniformity
2. Method and effectiveness of mixing, milling and blending
3. Weight, volume, density, density, porosity and uniformity of packing of stain batch for calcination
4. Calcining parameters-temperature, time, atmosphere, draft, type of fuel and type of crucible
5. Particle size and particle shape of the calcined stain

6. Testing, grading, controlling and blending of final stain

Ceramic stains in general are classified by application as follow:

1. Body stain

2. Glaze stain

**2.3.1 Body stain**

Mixing stains in body can be done in a variety ways but for best results the stains should be added to powdered dry body. The dry mix should then be made into a slip with water and allowed to soak for a few days. It should then be dried out to a workable consistency and wedged ready for use. The type of body will also have a profound effect on the color-white firing body giving purer colors and darker colored body giving more muted tones. In general, additions of 0.5-10 percent will produce a wide range. Body stains are stable and highly resistant to color change at high temperature. Basically, the structure of body stains is spinel structure or rutite structure. These are naturally occurring spinels which are combinations of alkaline oxide and amphoteric oxide such as alumina, manganese, chromium and iron. They have composition RO and $R_2O_3$ (R: standing for radical, O: oxygen). While, composition $RO_2$ such as titanium, vanadium, antimony and tin is rutites structure [13].

**2.3.2 Glaze stain**

Glaze stains are developed through the use of metals in some form. These forms may be oxides, carbonates, sulphates, nitrates, chlorides or even the basic metal itself. They may be used single or intermixed with other raw materials in various ways to achieve a desire stable color. They are often fluxes, clays or silica, resulting in colors that can not be made by the simple mixing to basic colorants.

### 2.3.3 Basic colorant materials

The mainly coloring resources are cadmium, chromium, cobalt, copper, gold, iron, magnesium, nickel, platinum, silver, titanium, uranium and vanadium. The potential of any colorant is subject to three main variables: first, the makeup of the glaze, particularly the fluxes used; second, the firing temperature; and third, the kiln atmosphere. The usage and color of basic colorant materials are shown in Table 2.3.

Table 2.3 Basic colorant materials [12,13]

| Element | Raw material | Color | Usage |
|---|---|---|---|
| Sb | $PB_2(SbO_4)_2$<br>$Sb_3O_4$ | Yellow<br>Yellow-Cream<br>Strong Yellow | Lead glaze, upto 1050°C<br>Low temperature glaze<br>Used with iron |
| Ba | $BaCrO_4$ | Bright lemon Yellow,<br>Yellow green, Green | Low temperature |
| Cd | CdS | Yellow, Orange, Red | Low temperature |
| Cr | $Cr_2O_3$ | Dark green<br>Orange, Red | Used with Co, Ni, Fe or Cu<br>Lead glaze, below 950°C |
| Co | $CoCO_3$ | Pale-Dark inky blue<br>Pink lilac, Purple blue | Lead glaze<br>Magnesium glaze |
| Cu | CuO | Green<br>Turquoise | Lead glaze<br>Alkaline glaze |
| Au | $AuCl_3$ | Pink, Purple | |
| Fe | $FeCO_4$ | Black | Both body and glaze, used with Co, Cu |
| | | Pink | Tin glaze, Oxidation |
| | FeO | Black | Used with Co, Cu |
| | $Fe_2O_3$ | Red, Yellow, Brown | Both body and glaze |

| Element | Raw material | Color | Usage |
|---|---|---|---|
| Mn | $MnCO_3$, MnO | Dark brown-Black | Body |
| | | Purple | Alkaline glaze, low temperature |
| | | Brown | Lead glaze |
| Ni | $NiCO_3$, $Ni_2O_3$ | Green | High magnesium glaze |
| | | Pink-Purple | High barium glaze |
| | | Blue | Used with Zinc |
| Ag | AgCl | Yellow, Pearl luster | Low temperature in reduction |
| Ti | $TiO_2$ | Yellow-Brown | In oxidation |
| | | Cool blue, Blue grey-Streaky purple | In reduction |
| V | $V_2O_5$ | Yellow, Blue | Body, with zirconium |
| U | $U_3O_8$ | Yellow | In oxidation |
| | $UO_2$ | Black | In reduction |

The advantages of ceramic stains are [14]:

1. Stability of color
2. Consistent and repeatable
3. Ability to target a specific color

**2.4 Literature review of waste utilization**

In recent years recycling of industrial wastes has been widely investigated because some wastes contain toxic metallic oxides which produce the environmental problems and recycling technology one of the solutions.

Hydrometallurgical zinc production generates jarosite, goethite and hematite waste which contaminated toxic metals such as lead, cobalt, cadmium and copper. Mainly zinc production is jarosite process. Jarosite waste has been used as raw material to produce construction materials such as bricks, blocks, cement and tiles.

Jarosite has been used as raw material with Portland cement or lime to improve the strength by hydration technique in amorphous gel form [15, 16]. Autoclave technique also has been studied; the leach liquor from this process was investigated. It found that counter current washing of the residue improved [17]. In Idia, sand and coal combustion residue was used as admixture to attain good workability and detoxify the toxic substance in the jarosite [18]. Beside of these techniques, Mario Pelino has studied conversion of jarosite to glass-ceramic by heat-treatment. Vitrification and crystallization under controlled thermal treatment improve the chemical debility [5, 19].

Goethite is another waste generated from zinc hydrometallurgical process similar to jarosite hence recycling of goethite has been concerned. Goethite has been used to produce glass and glass-ceramic [2, 4, 20]. Mechanical and chemical properties have been measured. The results indicate that glass and glass-ceramic production evaluated mechanical and chemical properties. Goethite has not only been studied in producing glass and glass-ceramic. But sintering behavior of it also has been investigated in the view of its low-cost reused as porous building materials for heat and sound insulation [1].

Besides the jarosite and goethite waste from zinc hydrometallurgical process, various kinds of waste such as granite waste, municipal solid waste and incinerator fly ash has been utilized. Granite waste is iron enriched residues compound by $SiO_2$, $Al_2O_3$ and $Fe_2O_3$ as major elements. In Brazil, granite waste has been used as raw material to produce blocks and tiles [21, 22]. The granite waste was characterized with respect to its mineralogical composition, particle size distribution and density. The results showed that the granite waste has physical and mineralogical characteristics that were similar to those of conventional ceramic raw materials. The properties of ceramic body such as bulk density, linear shrinkage, water absorption and mechanical strength were investigated. Ceramic body exhibited better values of water absorption and mechanical strength than the industrially used. Moreover, granite waste has been converted to glass-ceramic glaze with diopside frit. The effect of oxide content on the crystallization of diopside glass-ceramic was investigated. The results showed that the distribution of $Fe^{3+}$ ions among different crystalline phase such as franklinite ($ZnFe_2O_4$)

and hematite ($Fe_2O_3$) depends on the iron content in the original diopside mixture [23]. Italian botton ashes of municipal solid waste incinerators have been mixed with other wastes coming from metallurgical and mineral industrial waste to obtained glass-ceramic tiles. The tiles were prepared in air by a low-cost, low-temperature pressureless sintering process and were morphologically and mechanically characterized. The sintered materials were found to be good candidates for building applications [24]. Production of glass-ceramic from incinerator fly ash has been studied in Taiwan. This process was used to transform vitrified incinerated fly ash into a $CaO-Al_2O_3-SiO_2$ system of glass-ceramic products. The major phase exhibited is gehlenite ($Ca_2Al_2SiO_7$) which belongs to the melilite group. This glass-ceramic product has good physical and mechanical properties to serve as construction materials [25].

It is noticeable form most of works that construction materials produced from industrial wastes showed acceptable properties for the application.

This research was aim to utilize hydrometallurgical zinc waste as raw material in developing ceramic tiles and glaze in order to immobilize hazardous elements present in this waste. In case of developing ceramic glaze, zinc waste was used as color stain and for producing frit. For developing tiles, the use of high percentage zinc waste was more concerned and also zinc waste used for producing tiles does not need to be melted. The properties of ceramic glaze and tiles using this waste also investigated.