CHAPTER 2 LITERATURE REVIEWS AND THEORIES

2.1 Literature reviews and related patents

2.1.1 Literature reviews

In 2008, M. Hojamberdiev, *et al.* studied adsorption properties of materials from paper sludge by observing the adsorption of phosphate and methylene blue. Adsorbent samples can be prepared by three methods which are calcination, mechanochemical grinding and physical activation. They concluded that paper is low cost but highly effective adsorbent for eliminating harmful inorganic and organic ions from water [5].

In 2009, S.J.J.Lips, *et al.* studied water adsorption characteristics of kenaf. The yield of extracted bast fibres is below 1/3 of that of the kenaf stem weight. An important aspect for this application is the moisture absorption capability of the material. This paper claimed that water absorption of kenaf core particles is shown to be in the range of the other tested materials and the soft pith material showed very high absorbency [6].

In 2009, J. Vichaikosol studied the production of cat-litter from paper pulp and phosphogypsum which is by-product from the fertilizer industry. It was purposed to prepare cat-litter by varying amount of components and to find appropriate percentage of water for the cat-litter production by considering competency of pellet forming. There were 3 samples which their densities were lower than commercial product produced from bentonite. The obtained cat-litter densities were higher than commercial product produced from silica. Abrasion resistance of all obtained cat-litter was higher than both commercial cat-litter that results in lower dust spread. Although all obtained product had lower water adsorption ability, they were not easily broken after they adsorb water which is a desired competence for cat-litter [7].

2.1.2 Related patents

A method for producing liquid adsorbent by mixing gypsum plaster with water was proposed in US Patent 4163674. The process starts with mixing the gypsum plaster with water into paste form then pelletizing and then drying .The inventor revealed the volume of mixed water related to the bulk density and adsorption capacity characteristics[8].

US Patent 4264543 is the production of adsorbent granules which is produced from gypsum. This process starts by feeding plaster into a disc-granulator and then water is sprayed to the disc. The dry powder contact with water spray then forms to little balls and size growth caused by rotating of disc. Then, when they reach a size, they are discharged by centrifugal force. After that, moist pellet are fed into dryer. Because of pellet size distribution, the pellets might be screened to the desired size; the large pellet would be crushed and recycled. The product are ready to use as adsorbent materials for various purposes such as adsorbing of oil, grease a, other liquid and animal excrete [9].

US Patent 4821677 shows a method to produce animal-litter which produced from peanut hulls, peanut shells and finely ground natural mineral. The oil content of peanut shells acts like a binder in pelletizing. The mineral contributes ionic bonding for the nitrogen ions in animal excrete in order to reduce the odor of animal excrete [10].

A method to produce adsorbent from calcium sulfate is shown in US Patent 6029603. A binder such as clay, lignin and starch is added to calcium sulfate in order to help calcium sulfate pelletize. The produced adsorbent can be used as animal litter which can adsorb excretion of animal and its odor [11].

According to US Patent 6863027, it presents a method of making pellets of coconut coir pith used as cat-litter. The first step is to crush coconut husks, then mix the powdered coir pith with water. The mixture is compressed through a die for creating strings of coir pith, and then the strings are cut to little pellets. The pellets of coir pith are heated for removing moisture and hardening them. The patent is claimed that the coir pith core structure adsorbs urine and does not release any of urine smell to the atmosphere [12].

US Patent 20030070623 presents about making bio-degradable pet litter from coconut coir. The coconut coir can be used as pet-litter or in combination with other adsorbents namely clay, gypsum, wood chips, sawdust, paper, plastic or other similar materials. Coconut coir not only has low cost, it is an extremely adsorbent. Moreover, coconut coir has an ability to control and minimize odors of animal waste[13].

2.2. Theories

2.2.1. Cat-litter

Cat-litter is a material used as an adsorbent for cat's excretion. Cat-litter's function is to adsorb urine, moisture of feces and eliminate excretion odor. Characteristics of a good cat-litter are shown below

1) Good to adsorb liquid or moisture from excretion
2) Good to adsorb odor from excretion
3) Good to clump together when they are adsorbed
4) No dust

There are four different kinds of the most popular raw materials for cat litter which are:

1) Traditional clay based cat litter

This is the most common kind used and available at present. The clay minerals are very good absorbent and cat urine odors eliminator. The disadvantage of clay based litter is that it needs to be replaced frequently.

2) Scooping / clumping cat litter

This kind consists of bentonite clay. The benefit of clumping litter is that it does not need to be changed as often as traditional clay based litter. Bentonite clay clumps together when it is moist, therefore the cat owner can easily replace only the soiled litter. The whole contents of the cat litter box also need to be replaced on occasion but not frequently as the traditional type.

3) Crystal based / Silica gel cat litter

For the crystal based or silica gel cat litter, cat-urine-odor-control-capability is improved. Crystal based cat litter has the highest moisture absorbency and when stirred regularly, it only needs to be replaced once a month. The disadvantage of crystal based type is that it is often difficult to see when it needs changing and a puddle of urine will appear at the bottom of the litter box. The crystals form lumps which can be messy when it accidentally rolls underneath furniture. Some cats even refuse to use the crystal based type because of the lumpy texture and some cat owners fear that it might be unhealthy for their cat if it licks its paws after using its litter box.

4) Plant derived / Bio-degradable cat litter:

Advantages of bio-degradable type are that it is easy to flush and it is environmental friendly. Bio-degradable litter is not harmful to your cat's health and is low in dust thus it is ideal for asthmatic cats. This type can be made of wheat, peanut shells, wood shavings, corn cobs and other natural products. The only disadvantage of the bio-degradable type is the cost.

2.2.2 Phosphogypsum[14]

Phosphogypsum is a waste by-product from the fertilizer industries. Phosphogypsum is generated by the section of phosphoric acid production, raw material for fertilizer. In fertilizer industry, phosphate rock is processed by wet acid method, which is currently used over 90% of phosphoric acid production. Phosphogypsum production around the world is estimated to be about 100 – 280 metric tons per year. The main producers which generate phosphate fertilizers are located in the USA, the former USSR, China, Africa and the Middle East.

Phosphate ore can be processed either by dry thermal method or wet acid method. The dry thermal method produces phosphorus element by using an electric arc furnace. The wet chemical phosphoric acid treatment process, or called wet process, is widely used in phosphoric acid production. Dihydrate form of calcium sulfate ($CaSO_4 \cdot 2H_2O$) is generated in wet process as shown in eq(2.1).

$$Ca_5F(PO_4)_3 + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4 \cdot 2H_2O + HF \quad (2.1)$$

The wet process is economic but it produces a lot of phosphogypsum. It generates 5 tons of phosphogypsum while a ton of phosphoric acid is produced. Phosphogypsum is a moist, fine powder with free water content about 20 – 30 % and considerable amounts of impurities, the exact impurities and their amounts depending on the rock and the specific process. The impurities in phosphogypsum are H_3PO_4, $Ca(H_2PO_4)_2 \cdot H_2O$, $CaHPO_4 \cdot 2H_2O$ and $Ca_3(PO_4)_2$, residual acids, fluorides (NaF, Na_2SiF_6, Na_3AlF_6, Na_3FeF_6 and CaF_2), sulfate ions, trace metals (e.g. Cr, Cu, Zn and Cd), and organic matter as aliphatic compounds of carbonic acids, amines and ketones.

2.2.2.1 The $CaSO_4 - H_2O$ system[15]

The $CaSO_4 - H_2O$ system is characterized by five solid phases. Four exist at room temperature which are calcium sulfate dihydrate, calcium sulfate hemihydrate, anhydrite III, and anhydrite II. The fifth phase, anhydrite I, only exists above 1180 °C, and it has not proved possible to produce a stable form of anhydrite I below that temperature. Table 2.1 characterizes the phases in the $CaSO_4 - H_2O$ system. The first four phases are of interest to industry. Calcium sulfate dihydrate, $CaSO_4 \cdot 2\,H_2O$, is both the starting material before dehydration and the final product after rehydration.

Calcium sulfate hemihydrate commonly known as plaster of Paris is widely used in buildings, ceramics and medical industries. Hydration of hemihydrate is a highly exothermic reaction as shown in eq(2.2)

$$CaSO_4 \cdot 0.5H_2O + 1.5H_2O \rightarrow CaSO_4 \cdot 2H_2O + heat \quad (2.2)$$

In hydration, crystallization of gypsum occurs. When the gypsum is in paste form, the plaster sets and develops strength. The hardened mass is not a dense solid, but a highly porous material. There is a large internal surface consisting of interlocking crystals in the form of plates and needles. The microstructure of hardened gypsum pastes affects most of the physical and engineering properties particularly its rigidity.

Hemihydrate occurs in two different forms (α- and β-forms) depended on process; α-form is prepared by wet method and β-form is prepared by dry methods from calcium sulphate dihydrate. In the laboratory, β-hemihydrate is prepared from the dihydrate by heating under a low water vapour partial pressure whereas α-hemihydrate is prepared from the dihydrate under a high partial pressure of water vapour.

Table 2.1 Phases in the $CaSO_4$-H_2O system

Characteristic	Calcium sulfate dihydrate	Calcium sulfate hemihydrate	Anhydrite III	Anhydrite II	Anhydrite I
Formula	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 0.5H_2O$	$CaSO_4$	$CaSO_4$	$CaSO_4$
Molecular mass	172.17	145.15	136.14	136.14	136.14
Thermodynamic stability, °C	< 40	metastable in dry air	metastable in dry air	40-1180	>1180
Form or stages		Two forms: α β	Three stages: β-anhydrite III β-anhydrite III’ α-anhydrite III	Three stages: AII-s, slowly soluble anhydrite AII-u, insoluble anhydrite AII-E, Estrichgips	
Other names, often based on the application	Gypsum Raw gypsum Synthetic gypsum Chemical gypsum Byproduct gypsum Set gypsum Hardened gypsum FGD gypsum	α-form: α-hemihydrate autoclaved plaster α-plaster β-form: β-hemihydrate stucco plaster β-plaster plaster of Paris	Soluble anhydrite	Raw anhydrite Natural anhydrite Synthetic anhydrite Chemical anhydrite Byproduct anhydrite Calcined anhydrite	High-temperature anhydrite
Synthesis conditions:temperature, °C, and atmosphere	<40	α-form: >45,from aqueous solution β-form: 45-200 in dry air	α- and β-AIII: 50 and vacuum or 100 in air β-AIII’: 100 in dry air	200-1180	>1180
Production temperature, °C	<40	α-form: 80-180 β-form: 120-180	β-AIII and β-AIII’ : 290 α-AIII: 110	300-900, specifically AII-s: <500 AII-u: 500-700 AII-E: >700	Not produced commercially

2.2.3. Poly(vinyl alcohol) [16]

Poly(vinyl alcohol) (PVA) is a polyhydroxy polymer which is the largest-volume synthetic, water-soluble resin produced in the world. It is commercially manufactured by the hydrolysis of poly(vinyl acetate), because monomeric vinyl alcohol cannot be obtained in quantities and purity that makes polymerization to PVA feasible.

The main uses of PVA are in textile sizing, adhesives, protective colloids for emulsion polymerization, fibers, production of poly(vinyl butyral), and paper sizing. Significant volumes are also used in the production of concrete additives and joint cements for building construction and water-soluble films for containment bags for hospital laundry, pesticides, herbicides, and fertilizers. Smaller volumes are used as emulsifiers for cosmetics, temporary protective film coatings, soil binding to control erosion, and photoprinting plates.

Furthermore, PVA can be cross-linked using a multifunctional compound that reacts with hydroxyl groups. These types of reactions are of significant industrial importance as they provide ways to obtain improved water resistance of the poly(vinyl alcohol) or to increase the viscosity rapidly. The most commonly used cross-linking agents include glyoxal,glutaraldehyde, urea-formaldehyde, melamine-formaldehyde, trimethylolmelamine, sodium borate or boric acid, and isocyanates. Most of the reactions are either acid- or base-catalyzed.

Strongly chelating metal salts of copper and nickel such as cupric ammonium complexes, chromium complexes, and organic titanates and dichromates, can be effective insolubilizers for PVA. Heat treatment during drying of the PVA film or coating is generally sufficient to accomplish the cross-linking reaction. The dichromate reaction is catalyzed by ultraviolet light. Poly(vinyl alcohol), even when insolubilized by cross-linking, swells in water and loses strength on extended exposure. Complete water insensitivity cannot be achieved.

2.2.4 Plaster preparation [16]

Hemihydrate calciumsulfate($CaSO_4 \cdot 0.5H_2O$) can be prepared by calcinations of gypsum. There are two types of plaster which are α-hemihydrate or α-plaster, and β-hemihydrate or β-plaster. Two of them have different physical properties because of difference in their preparation. α-plaster is obtained from wet process but β-plaster comes from dry process.

1) α-hemihydrate or α-plaster

Three processing methods are used for the production of α-hemihydrate. One, developed in the 1930s, involves charging lump gypsum rock 1.3-5 cm in size into a vertical retort, sealing it, and applying steam at a pressure of 117 kPa (17 psi) and a temperature of about 123°C. After calcination under these conditions for 5-7 h the hot moist rock is quickly dried and pulverized.

Another method, first reported in the 1950s, has lower water demand. The dihydrate is heated in a water solution containing a metallic salt, such as $CaCl_2$, at pressures not exceeding atmospheric. A third method was developed in 1967, prepares very low water-demand a-hemihydrate by autoclaving powdered gypsum in slurry. A crystal-modifying substance such as succinic acid or malic acid is added to the slurry in the autoclave to produce large squat crystal

2) β-hemihydrate or β-plaster

The dehydration of gypsum, commonly referred to as calcination in the gypsum industry, is used to prepare hemihydrate, or anhydrite. Hemihydrate is generally called stucco in North America and plaster in many other continents. In North America, plaster is differentiated from hemihydrate or stucco by the inclusion of additives to control intended use properties such as rehydration time, density, coverage, strength, and viscosity.

β-hemihydrate can be synthesized by dry calcinations process. In this process, phosphogypsum is heated at 120-180 °c in dry air or vacuum condition. During the process, water vaporizes while crystallization of plaster are stopped so there are a lot of pore and low mechanical properties.

2.2.5 Size enlargement [17, 18]

Size enlargement is the process which small particles are put together to form larger masses in which the original particles can still be identified. Size enlargement is one of the most important steps in particulate solid process industries. Size enlargement is widely associated with agriculture, food and pharmaceutical industries and is an important role for mineral, metallurgical and ceramic industries.

There are several methods to enlarge size of particles which are granulation, compaction, extrusion, sintering, spray drying and prilling. Agglomeration is the formation of aggregates by sticking together of smaller particles. Granulation is agglomeration by agitation methods.

2.2.6 Adsorption[15, 16]

Adsorption is the phenomena which an ambient fluid phase adhere to the surface of a solid. This is a fundamental property of matter, having its origin in the attractive forces between molecules. This process generates a film of the adsorbate on the surface of the adsorbent. Desorption is a reverse process of adsorption.

Adsorption may be classified as chemisorption or physical adsorption, depending on the nature of the surface forces. In physical adsorption the forces are relatively weak which involving mainly van der Waals interactions. On the contrary, in chemisorptions, there is significant electron transfer, equivalent to the formation of a chemical bond between the adsorbate and the solid surface. These interactions are both stronger and more specific than the forces of physical adsorption and are obviously limited to monolayer coverage. The differences in the general features of physical and chemisorption systems are shown in Table 2.2.

Table 2.2 Parameters of Physical Adsorption and Chemisorption

Parameter	**Physical adsorption**	**Chemisorption**
heat of adsorption (ΔH)	low, or 3 times latent heat of evaporation	high, or 3 times latent heat of evaporation
specificity	nonspecific	highly specific
nature of adsorbed phase	monolayer or multilayer, no dissociation of adsorbed species	monolayer only may involve dissociation
temperature range	only significant at relative low temperatures	possible over a wide range of temperature
forces of adsorption	no electron transfer, although polarization of sorbate may occur	electron transfer leading to bond formation between sorbate and surface
reversibility	rapid, nonactivated, reversible	activated, may be slow and irreversible

2.2.6.1 The Langmuir isotherm[19, 20]

Langmuir proposed the first equation that relates the quantities of adsorbed gas to the equilibrium pressure of the gas. For this model, adsorption is limited to a monolayer. Langmuir's method is to equate the number of molecules evaporating from the surface with the number of molecules condensing on the surface. Because of short range of surface force, only molecules that strike bare surface are adsorbed. Then, molecules which strike previous adsorbed molecules are reflected back to the gas phase

2.2.6.2 The BET isotherm[19, 20]

The most important model in the study of adsorption is derived by Brunauer, Emmett and Teller for the multilayer adsorption of gases on solid surface. The multilayer adsorption theory, generally known as BET theory, has used in gas adsorption study and surface area measurement ever since. Brunauer, Emmett and Teller extended Langmuir's theory to multilayer adsorption. The BET theory assumes that the topmost molecules in adsorbed layer are in dynamic equilibrium with vapor. That means where the surface is cover with only one layer of adsorbate, an equilibrium exists between that layer and the vapor, and where two layers are adsorbed, the upper layer is in equilibrium with the vapor, and so on. Because the equilibrium is dynamic the surface may cover with many layers, but the number of molecules in each layer will remain constant. That is to say BET is based on the assumption that the forces that produce condensation are mainly responsible for the binding energy of multilayer adsorption.

2.2.6.3 Shape of isotherm[19, 20]

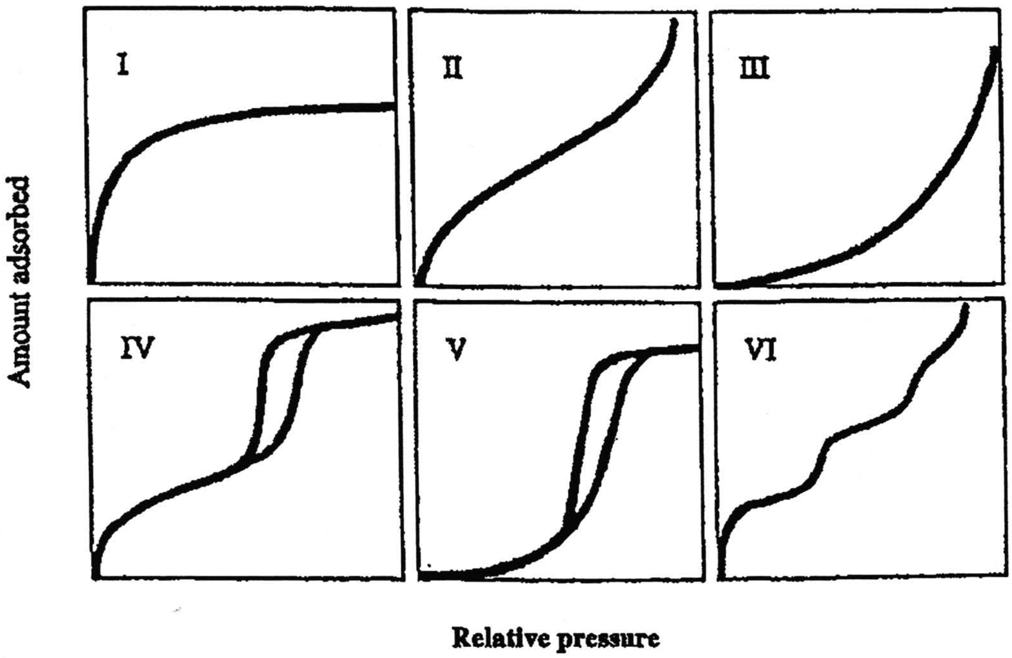

Figure 2.1: Shape of isotherm

Type I – Isotherm is characterized by a rapid initial rise in amount adsorbed at low pressure followed by a flat region. Pores are typically microporous with the exposed surface residing almost exclusively inside the micropores, which once filled with adsorbate, leave little or no external surface for further adsorption.

Type II - Most frequently found when adsorption occurs on nonporous powders or powders with diameters exceeding micropores. Inflection point occurs near the completion of the first adsorbed monolayer.

Type III - Characterised by heats of adsorption less than the adsorbate heat of liquification, adsorption proceeds as the adsorbate interaction with an adsorbed layer is greater than the interaction with the adsorbent surface.

Type IV - Occur on porous adsorbents with pores in the range of 1.5 – 100 nm. At higher pressures the slope shows increased uptake of adsorbate as pores become filled, inflection point typically occurs near completion of the first monolayer.

Type V - Are observed where there is small adsorbate-absorbent interaction potentials (similar to type III), and are also associated with pores in the 1.5 – 100 nm range.

Type VI – Isotherms arise with stepwise multilayer adsorption or noble gas molecules on a uniform substrate.

2.2.6.4 N_2 adsorption and desorption technique [21, 22]

N_2 adsorption and desorption technique is used to measure the surface area and porosity of the samples. It is an important technique for many types of advanced materials such as nanomaterials, pharmaceutical materials, powder metallurgy materials, battery active materials, fibers, pigments, etc.

At the beginning, molecules of the adsorbate gas are adsorbed on the sample surface, including the internal surfaces of pores, under the controlled conditions within a vacuum chamber. An adsorption isotherm is obtained by measuring the pressure of gas above the sample as a function of the volume of gas entered the chamber. The linear region of the adsorption isotherm is used to determine the volume of gas required to form a monolayer across the available particle surface area as described in the following equation:

$$\frac{1}{V\left[\left(\frac{1}{\varphi}\right)-1\right]} = \frac{c-1}{V_m c}(\varphi)+\frac{1}{V_m c} \qquad (2.3)$$

and

$$\varphi = \frac{P}{P_0}$$

where P = Equilibrium pressure of adsorbates at the temperature of adsorption

P_0 = Saturation pressure of adsorbates at the temperature of adsorption

V = Adsorbed gas quantity

V_m = Monolayer adsorbed gas quantity

c = BET constant

According to Equation 2.3, it can be plotted as a straight line as shown in Figure 2.2. The slope (A) and the y-intercept (I) are used to calculate the monolayer adsorbed gas quantity (V_m) and the BET constant (c) by Equations 2.4 and 2.5.

$$V_m = \frac{1}{A+I} \tag{2.4}$$

$$c = 1+\frac{A}{I} \tag{2.5}$$

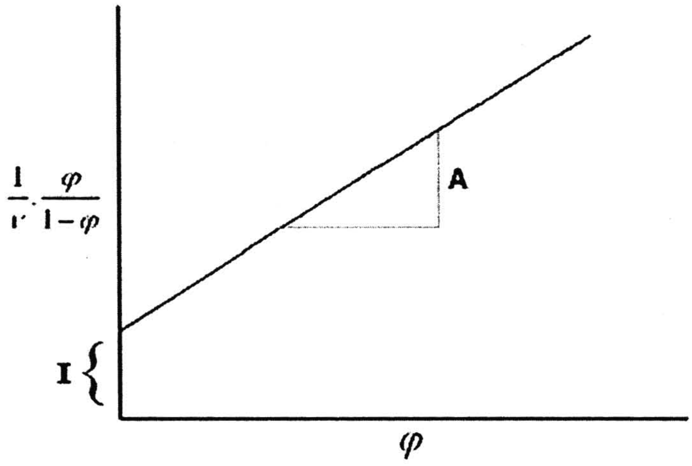

Figure 2.2 A BET plot [22]

A total surface area (S_{total}) and specific surface area (S) can be determined by Equations 2.6 and 2.7, respectively.

$$S_{total} = \frac{V_m N s}{V} \tag{2.6}$$

$$S = \frac{S_{total}}{a} \tag{2.7}$$

where N = Avogadro's number

s = Adsorption cross sectional area

V = Molar volume of adsorbent gas

a = Molar mass of adsorbed species

2.2.7 Assessment of surface area[19, 20]

Majority of methods for the surface area estimation of powders and porous materials depend on the measurement of adsorption(1916-1918). The coming of Langmuir's review of the nature of adsorption prompt several investigator to consider the possibility of using gas adsorption to determine the surface area. The first significant advances were made by Brunauer and Emmett(1935-1937) and their work was developed to the Brunauer-Emmett-Teller(BET) theory in 1938. BET method has become an utterly popular method for determining the surface area of adsorbents, catalysts and porous materials for the past 60 years.

2.2.8 Characterization of coconut coir pith [23]

Coir pith has very low bulk density and porous structure. Physico-chemical composition of coconut coir pith are shown as Table 2.3.

Table 2.3 : Characterization of coconut coir pith

Characterization of coconut coir pith	
bulk density	0.2 g/cc
calorific value	3400 kcal/kg
water holding capacity	460 vol%
lignin	30-35 wt%
cellulose	20-25 wt%
organic carbon	20-25 wt%
nitrogen	0.3 wt%
phosphorus	0.01 wt%
calcium	0.4 wt%
magnesium	0.36 wt%
iron	0.07 wt%
manganese	1.3 wt%
zinc	0.8 wt%