CHAPTER 2

LITERATURE SURVEY

2.1 The Thai Sanitaryware Industry[1]

Sanitaryware industry necessary acquires high technology in production process and experienced, skilled staffs. Thailand began to produce sanitaryware products in mass production since 1970. After that there are great improvement in production system and now Thailand has become outstanding sanitaryware producer in Southeast Asia.

In 1996 the production capacity was 155,800 metric tons from 8 sanitaryware factories that had the 4 eminent factories as Karat, Siam Sanitaryware, American Standard and Star Sanitaryware which consist about 123,000 metric tons or 79 % of total production, employed 7,000 staffs and workers.

Raw materials in sanitaryware industries are attained from local and imported raw materials.

Local raw materials are kaolin, ball clays, feldspar, silica sand, and plaster of Paris about 33.18 %.

Imported raw materials are stains, chemical reagents, ball clays, binders and pigments around 11.42 %.

And the importance costs of production are raw materials that have the great portion of 44.6 % total cost; the rest are depreciation and cost of labor. The following are the cost of sanitaryware production;

- Imported raw materials	11.42 %
- Local raw materials	33.18 %
- Energy	14.22 %

- Labor cost	14.22 %
- Depreciation value	15.98 %
- and others	10.98 %

The main problems in these industries are loss in process which can not be recycle because of the cost. Another one is non-consistency of the raw materials that effect so much on the cost. And the last is the labor turnovers including the qualification of the staffs.

The sanitaryware factories information have been shown in Table 2.1:

Table 2.1 Lists of names and production scales of Thai sanitaryware factories. (Unit: tons/year)

Factories	**Location**	**Labor**	**1982**	**1983**	**1984**	**1985**	**1986**
1. Karat	Saraburi	3,500	44,000	44,000	44,000	48,000	61,000
2. American Standard	Pathumthani Rayong	1,350	19,000	22000	24,000	24,000	24,000
3. Siam Sanitaryware	Saraburi	650	18,000	20,000	20,000	20,000	20,000
4. TCI	Samutsakorn	250	2,200	2,200	2,200	2,200	2,200
5. T. wattana	Samutsakorn	666	2,200	2,200	2,200	2,200	2,200
6. Siam Sanitaryware Industry	Saraburi	310	10,000	10,000	10,000	12,000	18,000
7. Star sanitaryware	Saraburi	N.A.	7,200	72,000	12,000	20,000	20,000
8. U.M.I. Laufen	Saraburi	225	-	-	-	-	8,400
Total		6,951	102,600	107,600	114,400	128,400	155,800

From: The Office of Industrial Economics.

We can conclude from this information that the importance factor of sanitaryware production is raw material and the dominant are ball clays that have the problem of consistency so we should study ball clays for characterization and consequently improvement can be successful.

Present Situation of Thai Sanitaryware(2)

Naturally, as ever, construction has been one of the more noticeable sufferers in the current climate, and although large scale infrastructure projects continue apace–such as Bangkok's traffic saving overhead railway–the private housing and commercial building sectors are feeling the pinch. Fortunately, in product quality and manufacturing technology terms, Thailand is still regarded quit comfortably as he regional leader in sanitaryware manufacture. Other areas of the ceramics sector may have had their advantages eroded by other countries – Indonesia's emergence in tiles is a prime example of this – but in sanitaryware, Thailand continues to hold on to its premier position. The benefits of this are critical. At a time when the domestic economy has slowed down, companies have at least been able to temper this decline by exporting significant tonnages.

As can be seen from the table 2.2, the total value of sanitaryware exports rose steadily from 1,364 m. Baht in 1993 yo 1,709 m. Baht in 1995, before slipping back to 1,615 m. Baht last 2 years – largely a result in a decline in exports to countries outside the East Asian region. In fact, if one considers sales to Asian countries alone, there has been a gradual increase from 1,022 m. Baht in 1993 to 1,168 m. Baht in 1996.

Table 2.2 Sanitaryware exports (m.Baht)

	1993	1994	1995	1996	1997 *
Hongkong	387.1	390.6	372.2	404.0	88.6
Laos	22.0	91.3	162.1	164.6	48.3
Taiwan	212.3	276.5	288.9	165.8	37.5
Japan	185.8	170.9	145.6	140.5	30.8
Vietnam	14.7	47.8	60.3	69.7	24.2
South Korea	168.0	50.4	59.8	90.0	23.0
Philippines	4.3	7.2	15.0	51.5	20.6
UK	72.1	52.8	88.1	71.5	19.4
Malaysia	17.6	19.8	34.9	39.6	9.9
Cambodia	15.2	47.6	34.6	53.5	8.0
Total	**1,099.1**	**1,155.2**	**1,262.1**	**1,250.9**	**310.7**
Others	264.7	442.7	445.9	363.9	58.2
Grand total	**1,363.8**	**1,598.0**	**1,709.1**	**1,614.9**	**369.0**

* January - March

The prospect of Thai sanitaryware

Presently, the major production techniques remain bench, battery and beam casting is gaining wider appreciation by reportedly providing a more consistent quality and higher level of output. However, whatever method is used, sanitaryware manufactures all fall back to one common denominator: fast casting. Quit why this should be the case is not certain. On one side, some manufacturers claim that they need to cast two to five times a day in order to maximize their capacity; whilst on yhe other side, some of the raw material suppliers point to the fact that production is currently down, and many moulds are not actually cleared that quickly.

Unfortunately, regardless of what is the correct position, the realities of the situation are neither here nor there: if the factories want fast casting rates, then it is more than likely they will have them, and this presents an ongoing challenge to the principal raw material suppliers to the region who must overcome the technical challenges posed by such demands. The perpetual desire for these faster rates is also likely to mean that there will need to be changes to body composition in the future, such as more permeable china clays, lower carbon ball clays and coarser ground, hard minerals. Provision of these more exacting mineral requirements is big business in Thailand, and it is a sign of the maturity of the ceramics industry in general that more sophisticated raw material grades are constantly being request.

2.2 Ball Clays used in Thailand

Sanitaryware industry deal with casting process of complicated- large shape, they have so many problems on forming, and consequently the outstanding properties that should be interested are casting properties. Now Thai sanitaryware industries are using monofiring that has short period of firing, so that another one property that should be aware of is the ignition loss of the body (as low as possible) because LOI can cause trouble on fast firing. Ball clays are the raw materials in sanitaryware that have most LOI, beside this, they also have high soluble salts (especially sulfate) and organic colloid that influence on rheology of casting slip. Consequently, ball clays seem to be the importance sanitaryware raw materials that should be studied to improve the overall workability.

From the literature, mentions were made on American and English ball clays because of their good properties. The American ball clays deposits at Tennessee and Kentucky lie in a broad plain at the northeastern edge of the Mississippi Embayment with rolling, gullied topography. These clays occur in both Holy Spring and the overlying Grenada formation of the Wilcox Group in lower Eocene time. The clay formations are interbedded with micaceous sand, ranging from fine to gravelly, evidently laid down during a period of heavy rainfall in a warm climate. The clay deposits occur in lenses like kaolins from Georgia and South Carolina. An important feature of these clays deposits is lignite, usually appearing as overlying seam of up to 10 ft. thickness or interbedded between clay seams. The color of ball clays is from adsorbed organic colloids which lend desirable forming qualities of ball clays. The mineral constituents of American ball clays range from 45-80 % disordered kaolinite, 4-20 % micaceous minerals, 10-30 % fine silica and 1-10 % organic matter.

English ball clays deposits lie in North and South Devonshire and in Dorsetshire; the clays being derived originally from the massive erosion of rock such as gneiss in the Welsh mountains. The feldspar and mica of these rocks decomposed to form kaolinite which was then transported by fluvial action to be redeposited to form shales near the present deposit areas. Volcanic activity led to granitic magma forcing their way up through the shales to form granite ridges; the broken overlying shales were then subjected to erosion and again transported by fluvial action to form the present ball clay deposits. The ball clay deposits of North Devon and South Devon are of late Eocene Age (20 million years ago) whear Dorset deposits were laid down in the middle Eocene (35 million years ago). The ball clays of South Devon have thin seams of lignite in between the beds of useful clays. North Devon ball clays contain (between 10-20 %) finely divided quartz. The Dorset ball clays also contain substantial amounts of micaceous substances (about 27-37 %), whereas in the Devonshire deposits the micaceous matter runs only 15-30 %; South Devon clays contain the least mica and the most clay substance.

In Thailand(3), ball clays can be separated to Northern, Middle and Southern parts, Northern part ball clays are Chiangmai ball clay for celadon and roofing tile industries. The others are Lampang ball clays in amphur Wang Nua, Mae Moh, Muang, Hang Chat, Jae Hom, and Mae Tha, the largest clay production areas are ball clays from Ban Jae Korn tumbol Thung phung amphur Jae Hom and Brown ball clay from Ban Mae Than amphur Mae Tha. Jae Korn ball Clay has fine grains slippery surface, high fired strength and white in fired color. Jae Korn is suitable for casting process.

Fig. 2.1 Jae Korn ball clay.

Mae Than ball Clay have variety of colors as white, yellow and deep brown. Some white and yellow Mae Than ball clays have little contamination of sand, are suitable to tile industries. Brown or Black Mae Than ball clay have more plasticity so fitting to produce sanitaryware and insulators.

Fig. 2.2 Mae Than ball clay mining.

Fig. 2.3 Mae Than ball clay.

Ball clay in the Middle and Eastern parts of Thailand are at tumbol Kok Mai Lai amphur Muang Prachinburi Province, are outstanding sources. The other is in amphur Makham Chantaburi province giving white in fired color but has small reserves.

Southern part ball clay , the importance one is Surat Thani ball clay that have been found in the areas of amphur Nasarn, Viensah, Kanchanadith and neighborly is Nakhon Si thammarat province in amphur Chawang, pipoon, Lansaka, Ron Phibun (tumbol Kok Kharm) and Sichon. The other provinces are Yala and Phuket.

Fig. 2.4 Kok Kharm ball clay from tumbol Kok Kharm amphur Ron Phibun Nakhon Si thammarat province.

Table 2.3 Chemical composition of some Thai ball clays.

Ball Clay Source Chemical Composition	Jae Korn Lampang	Mae Than Lampang	Kok Mai Lai Prachinburi	Na Sarn Surajthani
SiO_2	52.6	62.3	60.7	56.5
TiO_2	0.63	0.57	0.79	0.22
Al_2O_3	29.8	24.50	22.6	28.4
Fe_2O_3	2.09	1.22	3.50	1.88
CaO	0.40	0.24	0.15	0.31
MgO	0.74	0.59	1.05	0.31
K_2O	2.78	2.14	2.42	2.28
Na_2O	0.85	0.13	0.19	0.16
LOI	7.04	8.31	8.57	9.90

Table 2.4 Mineral composition of some Thai ball clays.

Ball Clay Source Mineral Composition	Jae Korn Lampang	Mae Than Lampang	Kok Mai Lie Prachinburi	Na Sarn Surajthani
Quartz (%)	15	28	18	5-6
Major	Very disordered kaolinite or Chlorite	Disordered kaolinite	Montmorillonite	Very disordered kaolinite
Moderate	Illitic mica	Illitic mica	Chlorite	Illitic mica
Minor	Hematite	Montmorillonite	Illitic mica and kaolinite	Feldspar

Table 2.5 Particle size distribution of some Thai ball clays.

Ball Clay Source Particle Size distribution	Jae Korn Lampang	Mae Than Lampang	Kok Mai Lai Prachinburi	Na Sarn Surajthani
+ 125 μm	0.21	3.1	N.A.	4.9
-20 μm	98	95	93	93
-10 μm	96	91	91	84
-5 μm	94	85	86	79
-2 μm	89	65	73	73
-1 μm	79	50	63	69
-0.5 μm	64	36	53	66

Table 2.6 Physical and rheology of some Thai ball clays.

Ball Clay Source Physical and Rheology Properties	Jae Korn Lampang	Mae Than Lampang	Na Sarn Surajthani
Vol. Drying shrinkage	34	23	29
MOR (PSI)	1996	748	1461
Fired color at 1200 ° C	25.6	87.0	54.2
Deflocculant demand (%)	1.25	0.85	0.90
at ball slip density	1.502	1.600	1.55
% Solid of ball slip	48.5	62.6	52.5

From unpublished information (from ball clay distributors), that sanitaryware industries use imported ball clays, SB-75 of WBB. Devon Clays Ltd. and Hycast of ECC International Ltd., but the largest portion are local ball clays.

From the literature the Thai ball clay that is used most for sanitaryware is Mae Than ball clay (deposit at Ban Mae Than tumbol San don Kaew, amphure Mae Tha, Lampang province). The outstanding properties of this clay are plasticity and good rheology. Besides these the seams of this clay laid between lignite seams; so it has more organic colloid and lignin humus that play the importance roles on rheology, good plasticity, easily slake when prepared to slip attaining good flow slip. Another clay is Jae Korn ball clay from Ban Jae Korn, tumbol Tung Phung, amphur Jae Hom, Lampang province that has cream fired – colore, is easy to slake and contributes plasticity to the slip. This clay has less sand and residue but the disadvantage is its high cost.

We can summarize that most of Thai sanitaryware procedures use imported SB-75and Hycast, and Mae Than local clay in their slip formulations.

2.3 Characterization of sanitaryware bodies(6)

A clay ceramic body, usually consists of more clays plus one or more nonclay mineral powders. Therefore, the many properties encounter in forming and firing of such a body are consequence of the interaction of two or more of a limited number of characterizing features. A classification of characterizing features was developed, to encompass all of the fired and unfired properties of body. Phelps identified what he called key features of working ceramic bodies, which could be used to design one in more quantitative methodology.

The five characterizing features are:

- Chemical Composition
- Mineral Phase

- Particle Size Distribution
- Colloids (surface areas)
- Colloid modifiers(Organic matter and soluble salts)

Any change in a contributing fundamental feature will in turn produce a change in a particular property, as each constituent of a particular clay body contributes proportionally to each of the five outlined characterizing features. All these characterizing features can be broken down into approximate 25 different items; however Phelps proposes reducing the list to eight to twelve which he called key indicators or points of emphasis, depending on the type of ware and its forming method. A key indicator is a characterizing property that must be matched or taken into consideration when doing a reformulation work. For sanitaryware bodies the key properties to control are:

- Plasticity (specific surface area, methylene blue index, percent less than 1 μm and organic content) always comes from ball clays.
- Dry strength (surface area and organic matter) that the resulting from the organic matter and fineness of ball clays.
- Vitrification (controlled by mole fraction of fluxes and fineness of fluxing components.)
- Glaze fit (which is affected by SiO_2:Al_2O_3 ratio, free quartz and particle size)

Phelps concluded that reformulation of vitreous sanitaryware casting bodies is done by manipulating those eight key indicators to established target values obtained from target bodies.

Summarizing, characterization has suggested ways in which the property-determining features of a material or body can be isolated and applied in controlling raw material and body properties.

2.4 Effect of Organic Matter on Ball Clay [(6)]

Major effects of carbonaceous matter are

(i) it imparts a dark colour to the raw material,

(ii) it may produce reducing conditions during kiln firing and so affect the colour and the vitrification behaviour,

(iii) it may reduce the amount of fuel required for burning the clay,

(iv) it may burn too rapidly in the kiln and cause over-vitrification and loss of shape,

(v) it may give rise to a 'black-heart' ,

(vi) its burn-out may increase the porosity.

Carbonaceous matter is sometimes deliberately added to a clay to produce desirable effects: (*a*) large particles of coal (up to pea-size) provide localised reducing conditions and, in some clays, give a pleasing appearance to the outside of facing brick made from them-about 5 per cent of coal by weight is normally added; and (*b*) finely-divided grains incorporated into a clay can provide sufficient heat on controlled burning to burn bricks completely without the need for additional fuel. This is the usual procedure in *clamp-firing*, where about 15 per cent of combustible is used –bricks of excellent colours are thereby produced if the clays have a sufficient proportion of iron compounds.

The presence of a proportion of low-rank carbonaceous matter, e.g. algae or oily constituents, is an advantage in some clays, because if the firing is carefully controlled, the organic components decompose steadily over a wide temperature range, thereby reducing the total fuel required and giving a more uniformly-fired brick. High-rank carbonaceous matter, e.g. bituminous and anthracitic coals, is not so desirable in clays, because it commences to burn only at high temperatures and then very rapidly, so that ware containing it tends to become over-vitrified.

If the carbonaceous matter is in the form of fine grains uniformly disseminated though the clay, it is not usually harmful, and is readily burnt out by slowly heating the clay in an oxidising atmosphere, care being taken to avoid surface fusion which seals the pores and prevents all the organic matter from being fully oxidised. Where larger masses of organic matter occur, however, it may cause trouble because of the amount of heat and gas evolved, causing superficial fusion, and because of the large cavities which are left when the particles of organic matter have been burned away. In all cases where a clay contains sufficient organic matter especially of a coaly or graphitic nature and sufficient fluxing materials, such as lime or soda compounds, the firing process is difficult to control and often results in the production of 'black heart', and sometimes of a highly bloated mass. These objectionable changes are due to the fact that the very close texture of some clays prevents the ready access of air to the interior of the articles, If much carbonaceous matter is present, before it can be oxidised and removed, the exterior pores of the article become closed with fused material and so effectually prevent the removal of the carbonaceous matter

2.4.1 Effect on casting property

It has been demonstrated that humic acids derived from various lignite sources vary widely in their effect on clay properties. Fig. 2.5 shows the effect of progressive additions of different humic acids on the viscosity of 20 percent weight solids suspensions of a hydrogen form Florida kaolin. Note that there was little if any change of pH, although viscosity was progressively reduced. The point at which organic color appeared in the supernatant liquid of centrifuge slurries signified the adsorptive limit for each humic colloid. Table 2.7 shows dry modulus of rupture values for solid cast clay-flint bodies where the Florida kaolin used had been treated with 0.5 percent additions of different humic acids. And if an organic-free clay is dispersed in a suspensions of humic acid colloids, there is almost instantaneous strong adsorption of the organic particles from the water by the clay and accompanying decrease in water of plasticity as shown in Table 2.8.

Table 2.7 Cast dry modulus of rupture.

Source of Humic acid	MOR. Psi
Untreated Florida Kaolin	276
English No.90 Ball Clay	423
Kentucky No.12 Ball Clay	621
Imperial Tenn. Ball Clay	577
North Dakota Leonardite	868

Table 2.8 Water of plasticity.

Treatment of Clay	Water of Plasticity (%)
Untreated Florida Kaolin	53.5
0.5 percent Eng.No.90 Humic acid	48.0
0.5 percent Ky.No.12 humic acid	46.0
0.5 percent Imperial Humic acid	47.5
0.5 percent N.D. Leonardite Humic acid	43.0

Fig. 2.5 shows the effect of progressive additions of humic acid colloid on the viscosity of a fine-grained, hydrogen-form kaolin slurry. Note that the changes in viscosity have all occurred with no alteration of slurry pH. It will be observed that humic acid colloids from different source-lignites have a wide range of deflocculating effectiveness. Those humic acids having high carboxyl group contents are stronger dispersing agents than those with high phenolic hydroxyl group contents. Ball clays may be thought of as fine-grained clays with humic acid colloids on the finest clay fraction.

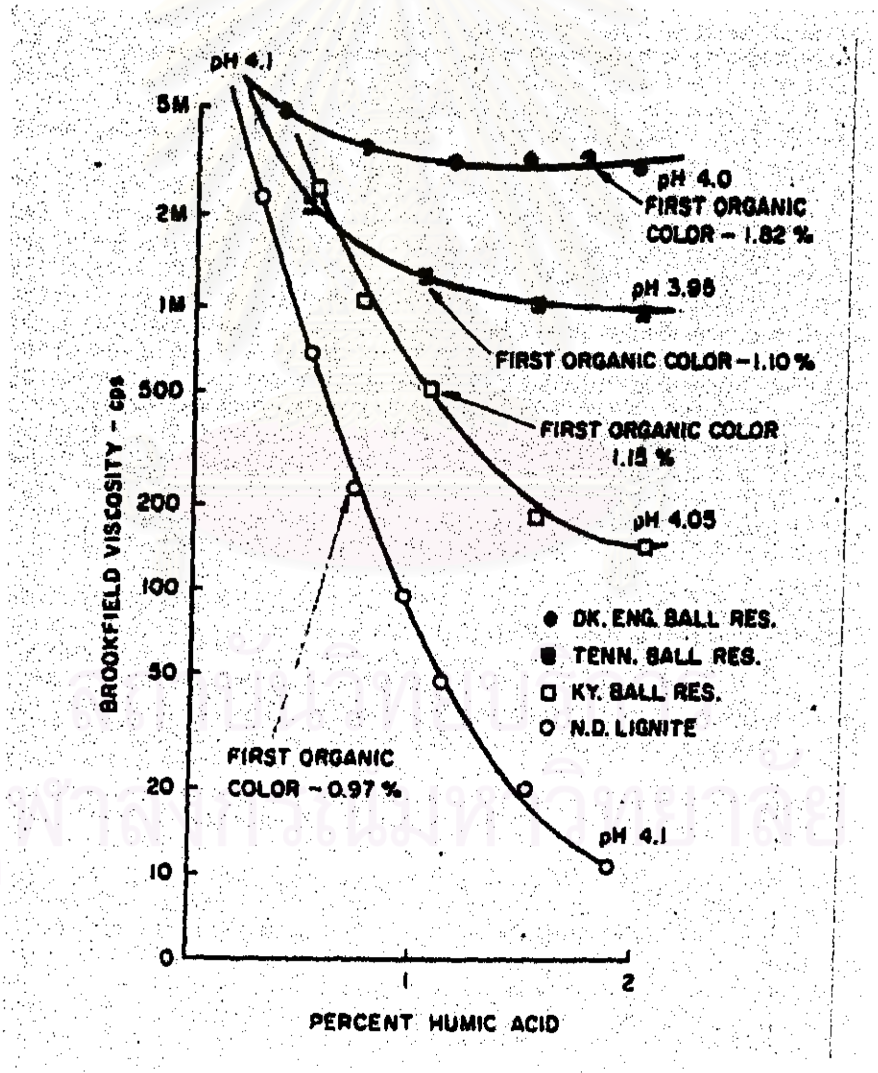


Fig. 2.5 Effect of humic acid additions on viscosity of 25 % Florida kaolin slurry.

2.5 Effect of Soluble Salts on Ball Clay

The soluble salts of ball clays may influence the plasticity considerably. Not only may the repulsive force between particles in the mass be altered as a result of cationic or anionic absorption but the surface tension of the liquid medium may be changed. Both effects have a pronounced influence on the plasticity of the clay mass. As an example of the former the action of alkalies and acids may be cited. When only 6 lb. of a mixture of sodium carbonate and sodium silicate is added to a ton of some kinds of clay, it can be made into a liquid with less than 20 per cent of its weight of water. If just sufficient acid is added to neutralise the 6 lb. of alkali, the whole mass becomes solid immediately.

The work of Speil and Sullivan and Graham(6) suggests that the greater the cationic concentration near the surface of the colloidal particle the more strongly will water be held. Small cations of high valency (e.g. Ca^{2+},H^{+},etc.) When absorbed will tend to give a higher proportion of bonded water than those of large size and small charge. In a plastic mass where the particles are very close, the absorbed water films around each colloidal grain merge together, so the force required to rupture such masses will depend on the degree of the water. The plasticity in terms of yield point and breaking strength in torsion are close to the theoretical predictions of the Hofmeister series as shown in Fig. 2.5. Because the water films surrounding clay particles are more flexible when alkali cations are absorbed, such clays are capable of greater deformation although they rupture more readily than do hydrogen or calcium clays.

More water is required to produce a plastic mass of a particular strength with a hydrogen and calcium clay than with one containing sodium as the exchangeable cations on the Yield Point and the Maximum torque of clay masses at various water contents cation; so for a particular water content, hydrogen and calcium clays require a greater moulding pressure, but the green body is stronger and less liable to loss of shape than sodium clays. In general, the range of water content over which the clay is workable is greater with a sodium than with a hydrogen or calcium clay although this is affected by other factors also.

The addition of a material which reduces the surface tension of water also liquefies a plastic mass. Such agents, which permit more concentrated suspensions to be used as casting slips, yet without introducing salts deleterious to refractory properties, are finding increasing use in industrial applications

The effect of soluble sulfate on casting process(8) is dosage of electrolyte or deflocculants in slip preparation. Decrease in soluble sulfate will reduce the content of deflocculants, while slip contain good flow at the same specific gravity. Such as we have 2 batches of slip at the same specific gravity at 1.77 (70 % solid), one batch has 400 ppm soluble sulfate and use 0.23 % deflocculants, where as the other has only 50 ppm soluble sulfate, deflocculant is reduced to 0.16 %. Excess soluble sulfate results brittle claycast and easy to peel and tear off when trimming and finishing its. Consequently from high sodium silicate cause brittle claycast. The slip that prepares from lower sulfate content can be fair cut. Nevertheless, direct prepared slip of sanitaryware process consist of organic colloid and deflocculant for rheology stability. Controlled soluble sulfate is required for flocculant element in flocculation in order to have good casting quality that means high casting rate, long casting range and plastic firmness of claycast.

2.6 Organic Matter in Soil Science(9)

The totality of organic matter in soil, except for materials identifiable as unaltered or partially altered biomass (plant part and microorganisms), is called ***humus***. This dark-colored constituent of the solid matter in soil plays a significant role in the formation of aggregates, in the control of soil acidity, in the cycling of nutrient elements, and in the detoxification of hazardous compounds. It comprises biomolecules, as well as the *humic substances*. In simple terms, humic substances are compounds in humus that are not synthesized directly to sustain the life cycles of the soil biomass. More specifically, they are polymeric compounds produced through microbial action that differ from biopolymers because of their molecular structure and their long–term persistence in soil. This definition of humic substances implies no particular set of organic compounds, relative molecular mass, or chemical reactivity. What is essential is a dissimilarity to biomolecular structure and an evolved, biologically refractory nature.

The biochemical processes by which humus forms are not fully understood, but there is agreement that four stages of development occur in the transformation of soil biomass to humus: (1) decomposition of the biomass components including lignin, into simple organic compounds; (2) microbial metabolism of the simple compounds; (3) cycling of C, H, N, and O between soil organic matter and the microbial biomass; (4) microbially mediated polymerization of the cycled organic compounds. The principal humus-forming compounds involved in stages 3 and 4 are believed to be a reactive class of compounds containing oxygenated benzene rings (quinones) that poly-merize readily.

2.6.1 Properties of Humic Acid and Fulvic Acid

The chemical properties of humic substances are often investigated after fraction of soil organic matter based on solubility characteristics. Organic material that has been solubilized by mixing soil with a 500 mol m^{-3} NaOH solution is separated from the insoluble material (termed ***humin***) and brought to pH 1 with concentrated HCl. The precipitate that forms after this acidification is called *HUMIC ACID*, whereas the remaining, soluble organic material is called *fulvic acid*. Repeated exteactions of this type are often done on the humin and humic acid fractions to enhance separation. The humic and fulvic acids recovered also are subjected to centrifugation and ion exchange resin treatments to remove inorganic constituents and biomolecules. The average chemical composition of soil humic and fulvic acids worldwide is summarized in Table 2.9. As a general rule, there is relatively more C and less O in humic acid than in fulvic acid. The average chemical formulas for these two fractions given were based on the composition data in Table 2.10. On the basis of a unit containing 1 mol of S, these formulas indicate that the average relative molecular mass of humic acid is larger than that of fulvic acid, which typically is <2000. Thus humic acid is relatively more polymerized than fulvic acid and therefore is at a more advanced stage of humification.

Table 2.9 also shows that fulvic acid contains more carboxyl groups par unit mass than humic acid. The total functional group acidity of humic substances is usually calculated as the sum of carboxyl and phenolic OH groups. Fulvic acid has the larger total functional group acidity, but both humic and fulvic acid possess a much larger dissociable proton charge per unit mass (6.7 and 11.2 mol kg^{-1}, respectively) than the typical cation exchange capacity of 2:1 clay minerals(<2 mol kg^{-1}). The implication of this fact for cation exchange in soils. The investigation of molecular structures in humic substances is a difficult area of current research. Although it is not currently possible to describe the molecular configuration of fractionated humic substances in any but the most general terms, the functional groups in humic substances-especially those most reactive with protons and metal cations have been characterized reasonably well. These include, in decreasing order of typical content: carboxyl, phenolic, and alcoholic -OH, quinone and ketonic carbonyl (C=O), amino, and sulfhydryl (SH)groups (Table 2.10). The prominence of the carboxyl and phenolic OH groups in this list underscores the significant acidity of humic acidity of humic substances. As shown in Table 2.9, Table 2.10, total functional group acidities (moles of dissociable protons per unit mass) ranging from 3 to 17mol kg^{-1} have been reported for soil humic substances across all terrestrial climatic zones. Since most of the total functional group acidity of humic substances dissociates between pH 5 and 7, humic and fulvic acid molecules are expected to bear a net negative charge in soils.

Spectroscopic and other physicochemical methods applied to humic substances have shown that there are four principal structural characteristics of humic and fulvic acids influencing their chemical reactivity.

1. Polyfunctionality: the existence of a variety of functional groups and a broad range of functional group

reactivity, representative of a heterogeneous mixture of interacting polymers.

2. Macromolecular charge: the development of anionic character on a macromolecular framework, with the resultant effects on functional group reactivity and molecular conformation.
3. Hydrophilicity: the tendency to form strong hydrogen bonds with water molecules solvating polar functional groups like COOH and OH.
4. Structuralability: the capacity to associate intermolecularly and to change molecular conformation in response to changes in pH value, redox conditions, electrolyte concentration, and functional group binding.

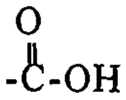
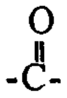
These properties of humic substances are common as well to biopolymers like proteins and polysaccharides, but in humic substances they reflect the behavior of a heterogeneous mixture of interacting polymeric molecules instead of the behavior of a structurally well-defined, single type of macromolecule. Thus the degree of complexity associated with these four properties is much larger for humic substances than for biomolecules.

Table 2.9 Average chemical composition of soil humic substances worldwide.

	C		H		N		S		O		COOH		Phenolic OH	
Substance	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**
	$g\ kg^{-1}$										$mol\ kg^{-1}$			
Humic acid	560	530-570	47	30-65	32	8-85	8	1-15	355	320-385	3.6	1.5-6.0	3.1	2.1-5.7
Fulvic acid	457	407-506	54	38-70	21	9-33	19	1-36	448	390-500	8.2	5.2-11.2	3.0	0.3-5.7

*Data compiled in M.Schnitzer and S.U. Khan, Soil Organic matter (Elsevier, Amsterdam, 1978).

Table 2.10 Important functional groups in soil humus.

Functional group	structural formula
Carboxyl	 $-\overset{\overset{O}{\parallel}}{C}-OH$
Carbonyl	 $-\overset{\overset{O}{\parallel}}{C}-$
Amino	$-NH_2$
Imidazole	Aromatic ring NH
Phenolic OH	Aromatic ring OH
Alcoholic OH	-OH
Sulfhydryl	-SH

2.6.2 Effects of Chemical Structure of Organic Matter on Rheology(10)

The chemical nature of the side groups of organic matter determines in part what liquids will dissolve the organic matter. Solubility in polar liquid of side groups are intermediate polarity in case of NaOH when preparing the slip. The chemical polarity and resulting affinity for a liquid is a necessary but not a sufficient condition for effecting solubility in liquid. The side groups of a molecule bond strongly to the side group of adjacent molecules, thereby giving the organic matter a high cohesive strength. The increase in viscosity of a liquid as large molecules (and colloids) are added is strongly influenced by their shape. The effectiveness of a molecule or colloid for increasing viscosity is dependent on its "sphere of influence" in the liquid. Molecules and colloids are constantly in motion (Brownian) because of thermal vibrations and impact by the liquid molecules. The solute molecules or colloids are tumbling and rotating, and the time-average volume swept out by molecules or colloids is defined as their “sphere of influence.” For a given molecular weight, a molecule has the largest sphere of influence when it has the largest length in one direction. Thus a linear molecule has a greater sphere of influence than a branched molecule of equivalent molecular weight. A fully extended linear molecule has a greater sphere of influence than the same molecule when it is coiled. The often dramatic increases in solution viscosity .