

PERFORMANCE STUDY OF A BASIC CHROME SULFATE PLANT

A THESIS

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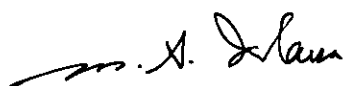
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We, the undersigned, certify that Md. Babul Miah, candidate for the degree of Master of Engineering (Chemical), has presented his thesis on the subject "PERFORMANCE STUDY OF A BASIC CHROME SULFATE PLANT". The thesis is acceptable in form and content, and the student demonstrated a satisfactory knowledge of the field covered by this thesis in the oral examination held on the April 18, 2000.



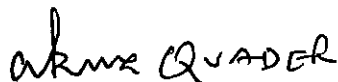
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ABSTRACT

The purpose of the present work was to study the performance of a Basic Chrome Sulfate plant located near Dhaka city. Basic Chrome Sulfate (BCS) is used for tanning purposes. The demand of this chemical depends on the quality of the product. This quality can be assured by controlling the process parameters. Process parameters determination, overall material balance of the plant and energy balance of the spray dryer were the main works of this study.

There are mainly two processes, by which BCS can be manufactured. But the present study was limited mainly to the sulfur dioxide reduction of sodium dichromate process. In the plant under study, sodium dichromate is imported from abroad and sulfur dioxide is supplied from a sulfuric acid plant located near the BCS plant.

In the above process the main process parameters that must be checked for quality control are: pH, percent of basicity, percent of Cr_2O_3 , unreduced chromium content, percent of Na_2SO_4 , and free SO_2 content in the product. These parameters were determined or checked at the laboratories of BUET and WATA Chemicals Ltd.

Experimental values were in the range of pH : 2.8 ~ 3.0, % Basicity: 34 ~ 37, % Na_2SO_4 : 24.3, and there were no free SO_2 and unreduced chromium in the BCS product. These results were found to be satisfactory from the viewpoint of commercial use of BCS for tanning. Results of product composition obtained from the overall material balance of the plant are in good agreement with experimentally determined values.

In addition, mass and heat balances of the spray dryer were carried out. Mass balance showed that the evaporation rate was within the specified range for the spray dryer.

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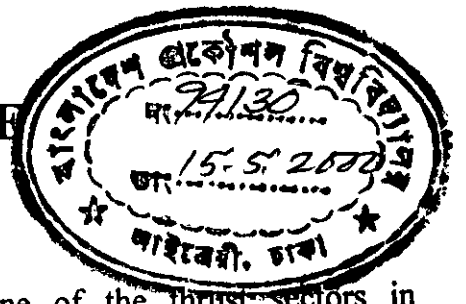
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CHAPTER - ONE

INTRODUCTION



Leather industry has recently been identified as one of the thrust sectors in Bangladesh, with a good potential for export. Leather is produced by tanning of animal hides using tanning agents. The tanning process transforms the protein collagen in animal hides into more stable product leather. Leather formed by tanning will resist water and moderate temperature in the moist state, and remain soft and flexible upon drying.

Leather tanning is carried out by two tanning processes: Vegetable tanning and Chrome tanning. Ninety percent of tanning is based on chrome tanning. Although, chrome tanning produces environmentally hazardous waste, still this process is extensively practiced in leather industry. Chrome tanned leather is popular with the consumers because of its lightweight, durability and resistance to heat and water. It is also easy to dye and finish. There is no wonder, therefore, that these properties should induce the leather manufactures to a steadily increasing use of the chromium compounds in the manufacture of various leathers, viz., clothing and gloving leathers, sole and belting leathers, textile and technical leathers.

Chrome tanning is the process of leather tanning with a Basic Chrome Salt (8). Usually Basic Chrome Sulfate (BCS) is used in the form of powder or solution. Chrome Sulfate containing (OH) group, is called Basic Chrome Sulfate. The BCS has basicity in the range of 33-58.3%, however, in industrial practice the basicity is maintained between 33%~37%. At this value of basicity, the BCS is soluble and a solution of 10 gm BCS in 100 ml of water has a pH close to 3.0.

Process of BCS Production

There are mainly two processes by which Basic Chrome Sulfate can be produced: Chromite Ore process and Sodium Dichromate process.

The process based on Chrome Ore is a long process. There are many unforeseen factors which may hamper its production. The quality of the product may not be up to the requirement when chrome ore is used; investment cost is also high due to higher battery limit area, higher storage area, a lot of equipment and machinery, higher manpower requirement. The chrome ore is not available in Bangladesh.

Sodium dichromate is an intermediate product on the way to production of BCS from chrome ore. If the intermediate product is used as a raw material, it makes the BCS production process simpler, less hazardous and product quality is easily attainable.

Less equipment cost and less skilled manpower make this process more attractive in this country.

In Bangladesh, a Basic Chrome Powder (BCP) plant first started functioning with Chrome Ore/Chrome fines as raw material. Within a very short period of time, a lot of problems were encountered in operating the plant. A new plant based on sodium dichromate as a raw material started production in 1997 and it is owned by WATA Chemicals Ltd.

Objective

This work deals with the study of the Performance of the Basic Chrome Sulfate Plant of the WATA Chemicals Limited and covers the following:

1. *Determination of the process parameters:*
 - PH
 - Basicity
 - Cr_2O_3 content
 - Unreduced chromium content
2. *Overall material balance of the plant*
3. *Energy balance of the spray dryer.*

CHAPTER – TWO

LITERATURE REVIEW

2.1 Leather Industries in Bangladesh

There are about 214 tanneries in Bangladesh. About 90% of the plants are located in Dhaka, 6% in Chittagong and 4% are scattered all over the country (1). The tanneries in Dhaka are located in an area called Hazaribagh.

Leather industry is one of the important export sectors in Bangladesh. This sector was the second in ranking in 1998 for earning foreign exchange.

Bangladesh has sufficient hides or skins to sustain large and healthy leather products industries. Annual availability of hides or skins includes 3.10 million pieces of cattle hides, 8.10 million pieces of goat skins, 0.16 million pieces of sheep skins and 0.07 million pieces of buffalo hides. Annual total supply of hides and skins will be about 160 million square feet, out of which only 15-18% is locally consumed and the rest is exported.

Leather industry in Bangladesh now exports crust and finished leather. Current share of finished leather export is only 15% and rest is exported as crust leather. Total export earning from leather industry was Tk. 6701.6 million in 1993-94, out of which Tk. 1075 million from leather products and rest from processed leather including finished and crust.

2.2 Tanning of Hides

The word 'tan' and its inflectional form tanning, which are derived from the Latin word for bark, are used to describe the process of converting the animal skin into the stable product leather (8). The action of tanning agents transforms the protein collagen in skins or hides into leather.

In a wider sense the easily putrescible hide substance is made resistant to microorganisms by tanning. Further, leather will resist water and moderate temperatures in the moist state, and remain soft and flexible upon drying. Tanning is carried out using mineral salts or vegetable tanning agents. The basic chrome sulfate is commonly used in tannery industry.

Leather Tanning Involves the Following Steps (2)

1. Salt or brine curing of hides before sending to tanneries.
2. Dehairing by lime treatment with a sharpening agent usually sodium sulfide.
3. Deliming and bating using ammonium sulfate followed by pickling with sulfuric acid.
4. Tanning using basic chrome sulfate usually of 33% basicity.
5. Finishing and drying.

2.2.1 Criteria of Tanning

There are two main criteria of tanning (9)

1. The first criteria of tanning potency of a substance is its capacity to form an irreversible combination with collagen, resistant to the action of water. Certain reactive protein groups are inactivated. However, the simple incorporation of an irreversibly fixed agent and the reduction of the water-binding capacity and the swelling tendency of collagen do not constitute or effect tanning.
2. The second criteria is the stabilization of the collagen by the tanning agent, improving its resistance to heat, proteinases, and swelling agents and preventing the "glueing together" of the fibers upon drying without detrimentally affecting the mechanical strength of the original hide structure.

2.2.2 Tests for Determining Tanning Criteria (9)

1. Shrinkage temperature of the leather in water.
2. The resistance of the tanned collagen in the moist state to attack by enzymes.
3. The chemical stability of the material upon storing.
4. The retention of the physical properties of the fibrous structure of the native hide particularly recognized as the degree of splitting up of the fibers.

2.2.3 Tanning Agents

The tanning agents are classified into two groups:

1. Mineral tanning agents, and
2. Tanning agents of organic nature.

In the first group, salts of heavy metals take a prominent place. The metallic compounds, mainly exerting tanning action by positively charged metal complexes, the most widely used tanning agent of the class is the basic chromium sulfate. Other metals in this group of cationic agents with tanning protency are aluminium, iron in the trivalent state and cobalt.

2.3 Chemistry of Chromium Salts and Chrome Tanning

The process of tanning hides and skins into leather with basic chromic salt is known as chrome tanning (8).

2.3.1 Chromium Salts

1. Chromium belongs to a group of elements known as trivalent. A typical oxide of trivalent Cr is chromium oxide, Cr_2O_3 .
2. Chromium can also act as a di, and hexavalent element producing CrO , and CrO_3 respectively as its oxides.

The properties of these oxides are as follows:

- CrO , Chromous Oxide: it is basic in nature and with acids gives rise to divalent salt. Chromous salts are very unstable and quickly oxidize into chromic salts.
- Cr_2O_3 , chromic oxide: it is amphoteric, i.e., behaves both as acidic and basic. With acid it gives rise to chromic salt and when fused with alkalis it give rise to chromites.
- CrO_3 , chromium trioxide or chromic anhydride is entirely acidic, combining with water to form an acid called chromic acid which produces salts with alkalis called chromates and dichromates. Chromium trioxide is also a very strong oxidizing agent. Dichromates are also oxidizing agents and in presence of an acid are reduced to chromic salts by both organic and inorganic reducing agents. In this reduction the hexavalent acidic chromium is changed into trivalent basic chromium.

Chromic salts such as CrCl_3 and $\text{Cr}_2(\text{SO}_4)_3$ are salts of the base chromic hydroxide, $\text{Cr}(\text{OH})_3$ which is a weak base, and normal salts of weak base hydrolyze when dissolved in water.

When chromic chloride reacts with water, basic chromium chloride and hydrochloric acid are formed.



When chromic sulfate reacts with water, basic chromium sulfate and sulfuric acid are produced.



Normal chromium salts, e.g. CrCl_3 and $\text{Cr}_2(\text{SO}_4)_3$, illustrated in Fig.1, have no tanning properties. In Fig.1, if, however, a slight portion of the acids formed by the above hydrolysis reactions are neutralized, then the residual basic salt exhibits slight tanning properties. Thus the tanning properties increase in proportion to the amount of neutralized acid. In normal salts of chromium, the three radicals are acid radicals,



Fig.1 Normal Chromium Salts with no Tanning Properties:

- (a) Normal chromic chloride
- (b) Normal chromic sulfate

It will be observed from the above hydrolysis equations indicated by equations (1) and (2) that in the formation of basic chromic salt a hydroxyl group (OH) is introduced in the molecule. It is possible, however, to have two or all of the acid radicals replaced by hydroxyl groups. The hydroxyl groups are called the basic groups. If one of the acid groups in the chromium salt is replaced by a OH group the compound thus formed is described as a basic salt. By adding increasing amounts of caustic alkali one can replace two or all of the acid radicals in the chromium salt by (OH) groups.

In Fig. 2, the addition of increasing amount of caustic alkali to the chromic sulfate liquors progressively increases the astringency of these liquors until they become turbid, and finally all the chromium is precipitated in the form of chromium hydroxide.

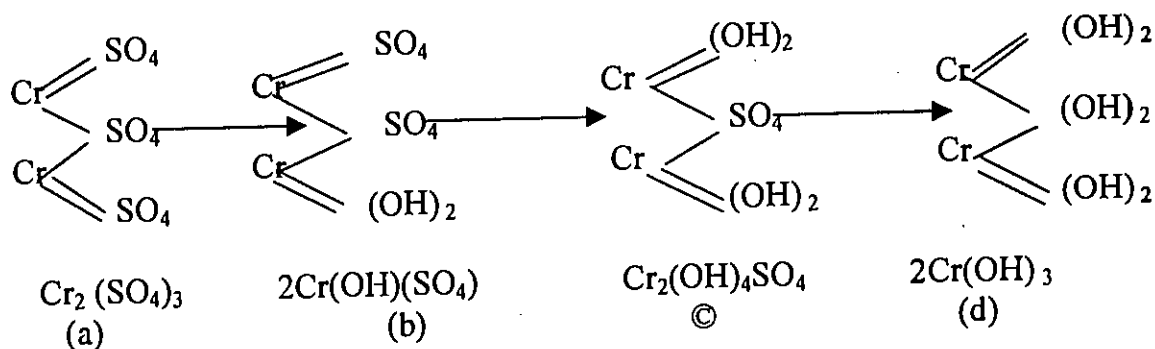
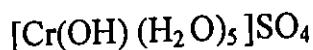


Fig. 2 Different Types of Basic Chrome Salts obtained by Reaction of Normal Chromic Sulfate with Sodium Hydroxide:

- a. Normal chromic sulfate, basicity 0 %
- b. Basic chromic sulfate, basicity 33.3%
- c. Basic chromic salt, basicity 66.7%
- d. Chromic hydroxide, basicity 100%

BCS with 33% basicity is commonly used in chrome tanning. Basic Chromium Salts contains one or more hydroxyl group. The degree of basicity increases with increasing number of (OH) group.

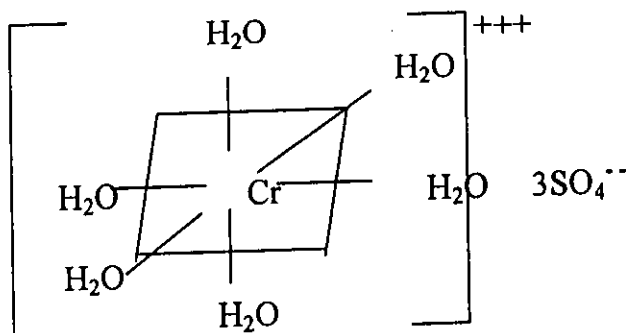
BCS used in tanning industry has the following formula:



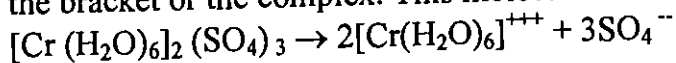
The Chromium atom in the above complex is hexavalent. The basicity of this complex is 33.3%.

Werner's Co-ordination Theory of Valency

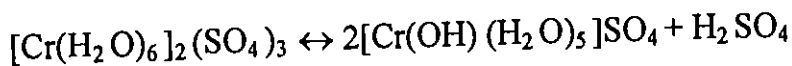
This co-ordination theory says that the chromium atom possesses two types of valencies: ordinary, and auxiliary or co-ordinative (8). Its ordinary valencies are 3 and auxiliary valencies are 6. By the 6 auxiliary valencies, a chromium atom can hold to it atoms, radicals, or co-ordinated groups forming with them a complex ion which is called chrome complex. In the hydrated chromium sulphate the three sulphate atoms are held by the ordinary and the 6 water molecules by the 6 auxiliary valences. Its formula is represented in the following way:



The 6 water molecules held by the auxiliary valencies of the chromium atom are shown within the large bracket of the above structure, forming a complex ion or chrome complex. The 3 sulfate ions held by the ordinary valencies are shown outside the bracket or the complex. This molecule so built up ionizes in the following way:

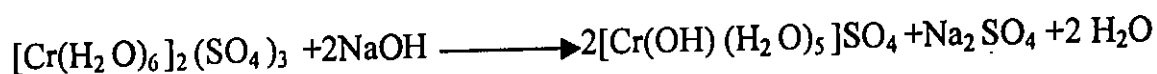


According to Werner's theory chromium sulfate, $[\text{Cr}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3$ formed is hexaquo which hydrolyses in aqueous solution as follows:



Hydrolysis is thus accompanied by the formation of free acid. The compound formed containing OH in the chromium complex is a hydroxo chromium compound. The hexaquo compound has no tanning action, because the hydroxo group so formed is unable to act as an ion and exhibits its basic properties owing to its close linkage with

the central atom. However, this compound can exhibit basic properties (tanning power) if hydrolysis is promoted by neutralisation of the free acid formed during hydrolysis. Thus, if an alkali is added to this normal salt, the acid formed in the hydrolysis is neutralized leading to increased hydrolysis, formation of basic salt and penetration of hydroxyl into the complex.



The hydroxo salt so formed (chromium compound which contains OH in the complex -basic chrome sulfate) can act as 'tan'.

2.3.2 Basicity of Basic Chrome Sulfate

The *Basicity* of chrome liquor, according to Schorlemmer (8), can be defined as "*the percentage valence of chromium attached to hydroxyl group.*"

All types of chrome compounds cannot tan protein. For this particular property the chrome compound must have hydroxyl group in the complex directly attached to the chromium atom. Such compounds are called *basic compounds*.

The basicity increases as more and more percent of chromium valence are attached with hydroxyl group. To understand this we will have to refer back to the scheme illustrated in the four different compounds of different basicities in Fig. 2

1. Compound (a) does not contain any (OH) groups, so it is 0% basic.
2. In compound (b) we find that 2 out of 6 valences of chromium (2 atoms of Cr) have combined with (OH) group and, therefore, this compound is 33.3% basic. $((1/3) * 100\%)$
3. Compound (c) contains 4 molecules of (OH) groups, so it is 66.7% basic.
4. Compound (d) however contains the maximum number of basic (OH) groups combined with the chromium and hence it is 100% basic.

When adjusting the basicity of chrome liquors with caustic soda the solution starts to become turbid at a basicity of 58.3% and hence the final basicity of the chrome tanning bath should be adjusted just below 58.3%. Percentage basicity is often called as % Schorlemmer.

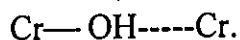
2.3.3 Olation of Basic Chrome Sulfate

Olation means the combination of two or more molecules of basic chrome compounds with one another and ultimately a bigger molecule is produced. Olation increases the size of the molecule of the basic chrome salts, converts their solution into semi-colloidal and colloidal condition (8).

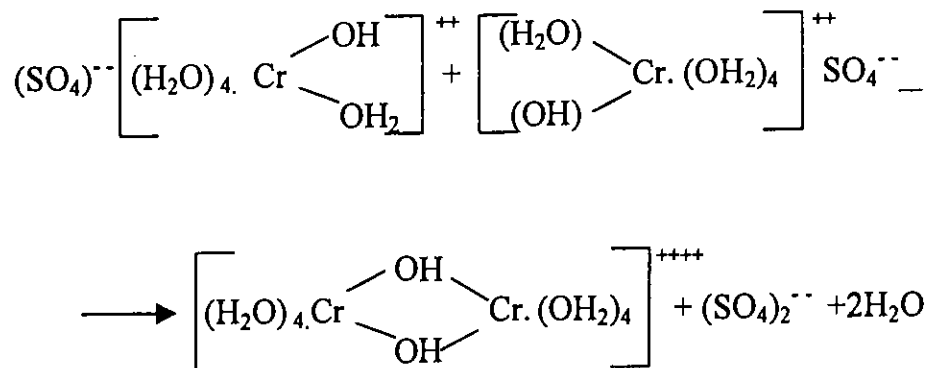
Olation and ageing increase the acidity of the chrome liquor. For that reason, it is common practice to age chrome liquor for few days just after its preparation. During this aging certain changes take place. Olation is one of them. Due to this olation the

molecular size of the chrome compounds increases which is needed within certain limit for the production of good chrome leather.

Finally olation can be defined as linking of one hydroxyl group by two adjacent chromium atoms (8). The hydroxyl group is linked up with one chromium by primary valence, and with next chromium by secondary valence, thus:



The mechanism of simple olation of 33.3% basic chrome sulfate is represented as follows:



The olated hydroxyl group is under the double influence of two chromium atoms, it is very firmly held in the complex and cannot be easily titrated with acid where as unolated hydroxyl group in the compound is titrable.

Factors Which Increase the Degree of Olation

The degree of olation is increased by rise of temperature, concentration of chrome in the liquor, rise of basicity of the liquor and time that have already been mentioned in the topics of olation. These effects are illustrated by the following tables. This information is based on the work of Stiasny and his collaborators (8):

1. Influence of temperature on the of olation of 33.3% basic chrome sulfate of 1% Cr content in one hour after the preparation of the liquor:

Temperature	Degree of olation
At room temperature	16.6
At 40 ⁰ C	84.3
At 75 ⁰ C	98.5

2. Influence of chromium concentration on degree of olation at 75°C after one hour of the preparation of liquors of 33.3% basic chrom sulfate liquors:

Concentration of Cr	Degree of olation
0.1%	92.9
0.2%	95.6
0.5%	97.3
1%	98.5

3. Influence of basicity on degree of olation at room temperature after an hour of the preparation of the liquors:

Basicity of liquor	Concentration of Cr	Degree of olation
33.3%	1%	16.6
50%	1%	37.7

4. Influence of time on the degree of olation of 33.3% basic liquor of 1% Cr content at room temperature:

Hours	Degree of olation
After 1 hour	16.6
After 5 hours	62.5
After 24 hours	79.7
After 5 days	89.3
After 4 weeks	93.2

2.3.4 Properties of Chrome Liquor

- *Effect of pH value in chrome tanning*

If the pH value of the chrome tanning liquor increases the molecule of the chromium salt become larger and larger thereby reducing the rate of penetration of the tan liquor into the skin. Chrome liquor with a high pH value may therefore cause over tannage of the outer layer of the skin resulting in drawnness of the grain. The pH value of chrome liquor changes upon the addition of acid or alkali. The pH value of chrome liquor varies also as a function of ageing, heating of the liquor or upon the addition of natural salts.

Acid lowers the pH value and alkali increases the pH value. So when free acid, present in the chrome liquor penetrates the skin more readily than the basic chrome

salt, thereby the chrome liquor, will become more basic and more colloidal due to hydrolysis. Since pH is most important factor for tanning, pH must be measured and fixed accurately at about 2.8.

- ***Effect of Concentration***

When chrome liquor is diluted, the basic chromium compound is hydrolyzed and thereby the basicity and molecular size of the chrome complex increases even though it does not affect the basicity of the liquor as a whole. The pH of the liquor does not appreciably decrease due to dilution even though free acid is released due to hydrolysis of chromium salts. This increase in astringency of chrome compound due to dilution may harden the grain due to over tanning if diluted liquor is used at the beginning. Thus the quality of finished leather may change due to use of dilute liquor at the start, instead of fairly concentrated liquor.

The electrical charge of the chrome is also changed with dilution. The acid group in the complex, if any, is replaced by water molecule due to dilution and therefore the complex becomes more electro-positive. If the original acid groups in the complex be oxalate, formate etc. whose affinity for chromium is more than water, these types of electrical change will not occur.

The amount of Cr_2O_3 uptake by collagen is also dependent to concentration. It has been observed by users that the chromium fixation by the hide portion increases with the increase of liquor concentration up to a limit after which the chromium fixation decreases with the increase of concentration. This statement is correct only when there is neutral salt in the liquor. Salt and acid free chrome liquor does not show such decrease in chrome fixation after a particular degree of concentration.

- ***Effects of salt in chrome tanning***

1. **On the chrome liquor are:**

- a. To lower the pH value
- b. To increase the real concentration of the chrome liquor
- c. To affect the nature of chrome complex
- d. To change the precipitation figure of the chrome liquor

2. **On the leather are:**

- a. To change the chrome fixation by the collagen
- b. To change the shrinkage temperature and other qualities like fell, fullness etc. of the leather.

The increase in concentration and the lowering of pH value of the chrome liquor, when neutral salts are added is, as is believed now-a-days due to the association of large number of water molecules with the salts.

When some amount of salt is added to chrome liquor, the acid portion of the salt penetrates into the chrome complex by displacing some groups, whose affinity for chromium is less than the penetrating acid group. Thus the available balancing of chromium for the oxygen atom of the hydroxyl group, present in the complex, is lessened and consequently the effect of oxygen upon the hydrogen of the same hydroxyl group increases. The hydrogen, therefore, cannot readily co-ordinate with the active group of the collagen i.e. the astringency of the chrome liquor decreases due to the addition of the salt. To activate all the active groups of the collagen, therefore, more chrome complexes will be needed i.e. the Cr_2O_3 fixation by collagen should increase. In dilute chrome liquors, where the presence of salt is very small, this type of increased chrome fixation has been repeatedly observed. But in the case of concentrated chrome liquor, where sufficient salt is present, reverse result is obtained, perhaps, due to the shrinking action of the salt.

Since the astringency of the chrome liquor is decreased by the addition of salt, the danger of over tannage of the grain by the liquor of high basicity is reduced when small amount of salt is added. The leather, therefore, contains more chrome without any hardening effect of the grain. The leather thus becomes full and of finer grain and of good feel.

- *Effect of basicity on pelt*

If the basicity is increased, the number of OH groups in the chrome complex will be increased and then olation and size of the chrome complex will be increased. The rate of penetration of the chromium into the pelt is slowed down because of the increased size of the chromium complexes, the precipitation figure is decreased, the pH value of the liquor increased and there is a corresponding decrease in the swelling power of the liquor. For practical purposes, the basicity depends upon the kind of pelt, the type of leather to be produced, previous treatment of the pelt, the nature of the processes after tanning, the kind and concentration of the chrome liquor and its content of neutral salts. Too low a basicity gives an empty, flat, hard, tinny leather with a tender grain. Too high a basicity overloads the fibers with tan and particularly the grain, resulting sometimes in a cracky grain and in an under tannage of the middle layer. Since the basicity is the most important factor in tanning processes, so, basicity must be fixed at a particular value. In tanning industries, BCS with 33.3% basicity is usually used.

- *Piling up after tanning*

Since the fixation of chromium compounds to pelt does not become complete in the tanning drum, the chrome blue must be aged in the piled condition on the floor at least for over-night. Some tanners horse up the leather at this stage and do not get the full benefit of aging due to removal of loose chromium with water that drips out from the horsed up leather. If pleat or fold remains in a piece of leather in a pile, the loose chrome liquor is forced away from the folded portion or unfolded regions and gets fixed there. Thus the chrome content in the folded area of tanned leather will be less than other regions. For this uneven distribution of chromium fold marks generally develop.

2.4 Environmental Effects and Treatment of Tannery Effluents

A serious environmental degradation is caused by tannery industries if proper operation and manufacturing processes are not followed. The sludges from the chrome tanning operation are hazardous in nature since these sludges contain almost all the chromium that remains unutilized in a tannery. According to the ESCAP guide-lines on pollution control in tannery industry (3), the spent chrome tan liquor is greenish in color and highly acidic. This is considered as a waste. The waste contains a high concentrated of trivalent chromium ranging from 100 to 200 mg/l. BOD of this waste is usually about 1,000 mg/l.

It is known that trivalent chromium is nontoxic while hexavalent chromium is toxic (5). Hexavalent chromium is not present in the waste chrome liquor because of the reduction agent is used and one-bath-process utilized (3). There is a maximum permissible limit of chromium for the discharge of the tannery effluent into land or water bodies. This limit can be attained by proper treatment of the tannery effluent.

The treatment of tannery wastes consists of the primary and secondary treatments. The primary treatment is carried out for removal of larger solids and equalization of the beam house wastes and tan house wastes. In primary treatment 80-90% of the solids are removed by sedimentation. The secondary treatment also called the biological treatment uses trickling filter or activated sludge process, resulting in 90% BOD reduction. The sludge from this step is dried on drying bed and used as manure (7).

From environmental viewpoint, the state of tannery industries in Bangladesh is bad. At present most of the tannery industries in Bangladesh discharge tanning waste without treatment to the neighboring land and/or water bodies. For example, wastes from 170 tanneries at Hazaribagh are discharged untreated into the Buriganga River. Average concentrations of some environmental parameters in tannery effluent discharged to Buriganga River from Hazaribagh area is shown in Table 1 (1). It can be seen from this table that the range of values of BOD, COD and chromium in discharges into Buriganga River is very high compared to the permissible limits.

Table 1 Concentrations of Tannery Effluents
(Data for the period of January - June, 1989)

Parameters	Range of values	Permissible limit
Biological Oxygen Demand, BOD (mg/l)	120 - 3,000	30
Chemical Oxygen Demand, COD (mg/l)	187 - 3,200	250
Chromium (mg/l)	5 - 40	1

2.5 Manufacture of Basic Chrome Sulfate (BCS)

Basic Chromic sulfate is manufactured as a product under various trade names for use in leather tanning. It can be manufactured from Chrome Ore involving two steps such as sodium dichromate production and its reduction to basic chrome sulfate. There are two reducing agents commonly used: sugar and sulfur dioxide, though other organic materials have been used during sugar shortages.

The BCS compounds are sold on a specification of chromic oxide, Cr_2O_3 content and basicity, the latter value referring to the degree to which the chromium is converted to the theoretical hydroxide. Thus $\text{Cr}(\text{OH})\text{SO}_4$ is 33.3% basic. The Cr_2O_3 content of solid chrome tanning compounds ranges from 20.5 to 25%, and basicity ranges from 33 to 58.3%, and at WATA Chemicals Ltd. this range is 33~37%.

2.5.1 Sodium Dichromate Production from Chromite Ore

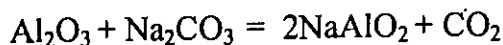
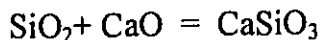
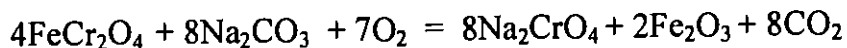
Chromite ore is used as raw material for production of sodium dichromate. Chromite ores are available in different ranges, whose compositions are shown in table 2.

Table 2 Typical Range of Analysis of Chromite Ores Constituent (%)

Country	Cr_2O_3	FeO	Al_2O_3	MgO	CaO	SiO_2
USSR	39-56	11.5-14.1	9.5-17.5	13.3-16.1	0.5-1.5	5.8-9.4
South Africa	42-51	24.7-34.2	12.0-15.0	9.5-13.0	0.0-1.0	1.5-5.0
Turkey	37-49	14.0-15.2	13.0-24.4	16.5-17.7	0.2-1.0	4.0-5.0

The block diagram for production of sodium dichromate from chromite ore is illustrated in Fig. 3.

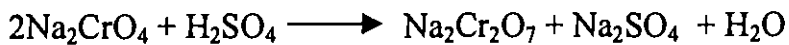
Soda ash and lime are mixed with Chromite Ore powder and then it is calcined in a horizontal cylindrical Rotary Kiln provided with a constantly fired burner. The reaction temperature is kept between 1000°C and 1100°C inside the Kiln. As the solid mass travels across the length of the Kiln at first gets dried and is then preheated in the preheating zone of the Kiln (4). Thus the mass travels slowly towards the other end of it. In reaction zone the following reactions take place simultaneously in the oxidizing atmosphere of the Kiln.



From the above reactions it is clear that higher the alumina content of the Ore, the higher is the soda loss. Formation of fused sodium aluminate and calcium silicate

produce lumps and create agglomeration of the products of reactions. This phenomenon prevents yield of the product due to the absence of required granulometry and improper mixing of the reactants, sometime forming fused mass adhering to the brick lined surface of the Kiln. Yield of Sodium Chromate under ideal operating conditions is expected to be 90%. Later this product is cooled in a rotary cooler at around 100-150⁰C. It is then taken to leaching tank for recovery of soluble Cr₂O₃ in hot water at 60-70⁰C as sodium chromate solution.

Sodium chromate solution at 40% concentration is oxidized by sulfuric acid to get sodium dichromate. The conversion of sodium chromate to sodium dichromate is represented by (5):



The sodium sulfate solubility is low in sodium dichromate solutions, thus producing sodium sulfate crystals during the reaction. Sodium sulfate in the mother liquor is filtered to get sodium dichromate solution and sodium sulfate separately.

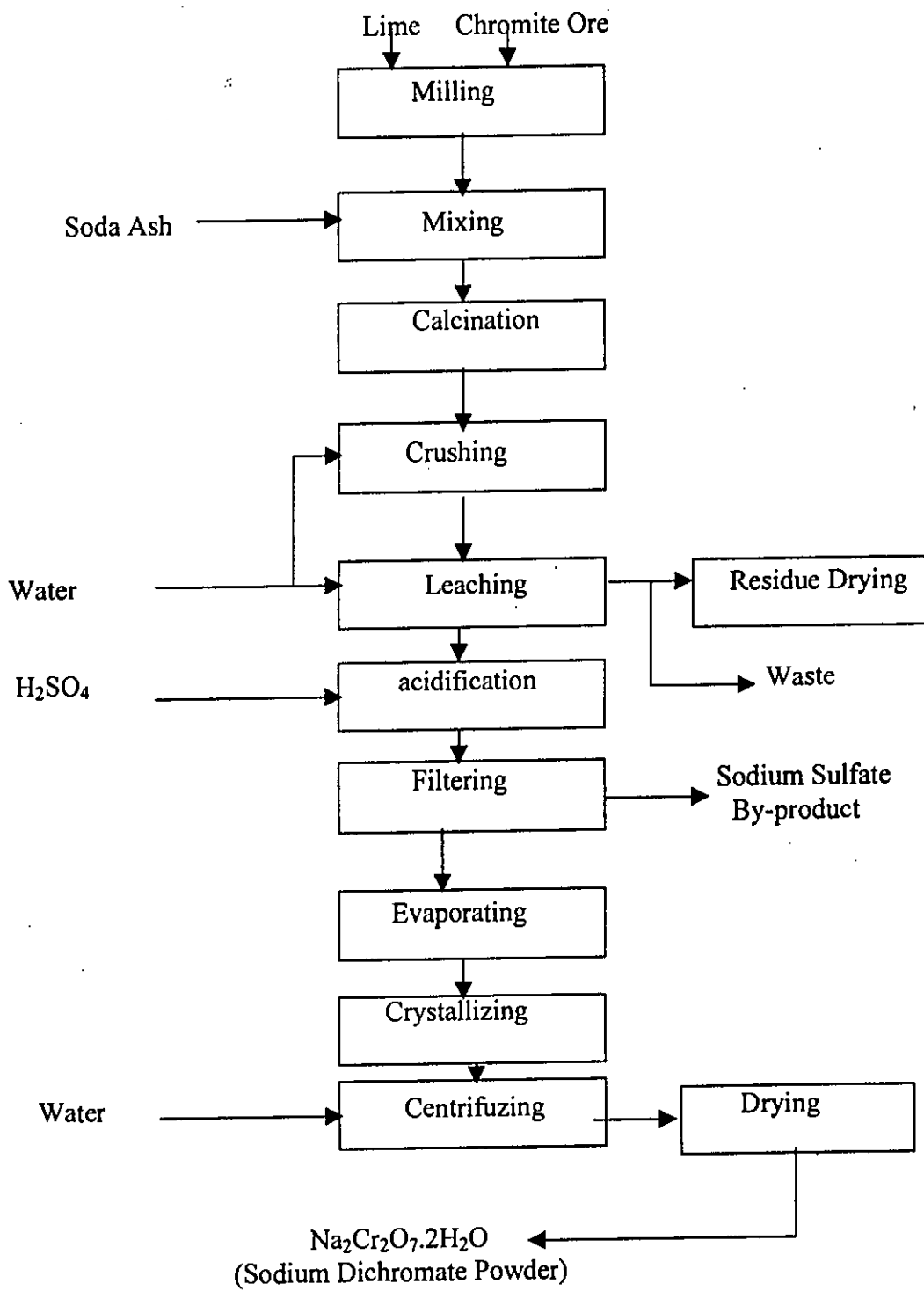


Fig. 3 Block Diagram for Production of Sodium Dichromate (5)

2.5.2 Major Types of Process for BCS Production

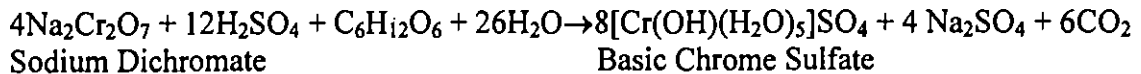
2.5.2.1 Sugar Reduction Process

2.5.2.2 Sulfur Dioxide Reduction Process

2.5.2.1 Sugar Reduction Process

Sodium dichromate solution is added with sugar for reduction by using the stoichiometric amount of sulfuric acid in an agitated acid resistant tank. The reaction is highly exothermic and must be carried out with care to prevent foaming and boiling over. The reaction is completed by boiling(2).

Theoretically, glucose is oxidized to CO₂ and water.

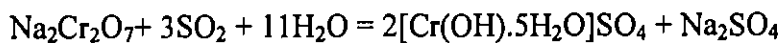


However, not all the glucose is oxidized, nor does the formula given represent the exact state of the chromium complex because hydrolysis, polymerization, and entrance of sulfate into the complex occur. Glucose or molasses-reduced chromium salts produce a leather of increased fullness with uniform chrome distribution throughout the thickness of the hide. It is now known that this difference in the tanning behavior is related with the formation of organic bye-products (formic acid, oxalic acid) during the reduction of dichromate- acid mixture with molasses or glucose.

2.5.2.2 Sulfur Dioxide Reduction Process

In this case, Na₂Cr₂O₇ is reduced by SO₂ and a 33.3% Basic Chromic Sulfate is automatically obtained. A block diagram is illustrated in Fig.4.

The reaction taking place in the chrome solution tower is as follows:



Pure sulfur dioxide is bubbled through the sodium dichromate solution in an acid-resistant tank, whereas burner sulfur gas is passed through a ceramic-packed tower countercurrent to descending dichromate solution. After reduction is complete, steam is bubbled through the solution to decompose any dithionate that may have formed, and to remove excess sulfur dioxide.

After reduction, any desired additive such as aluminum sulfate, is incorporated, the solution is aged. It is then spray dried. Careful temperature control during drying is necessary to obtain a highly water-soluble solid product.

Basic Chrome Powder can be manufactured either from chrome ore or an intermediate product sodium dichromate. On the other hand sodium dichromate is manufactured from chrome ore. But in our country sodium dichromate is imported from abroad.

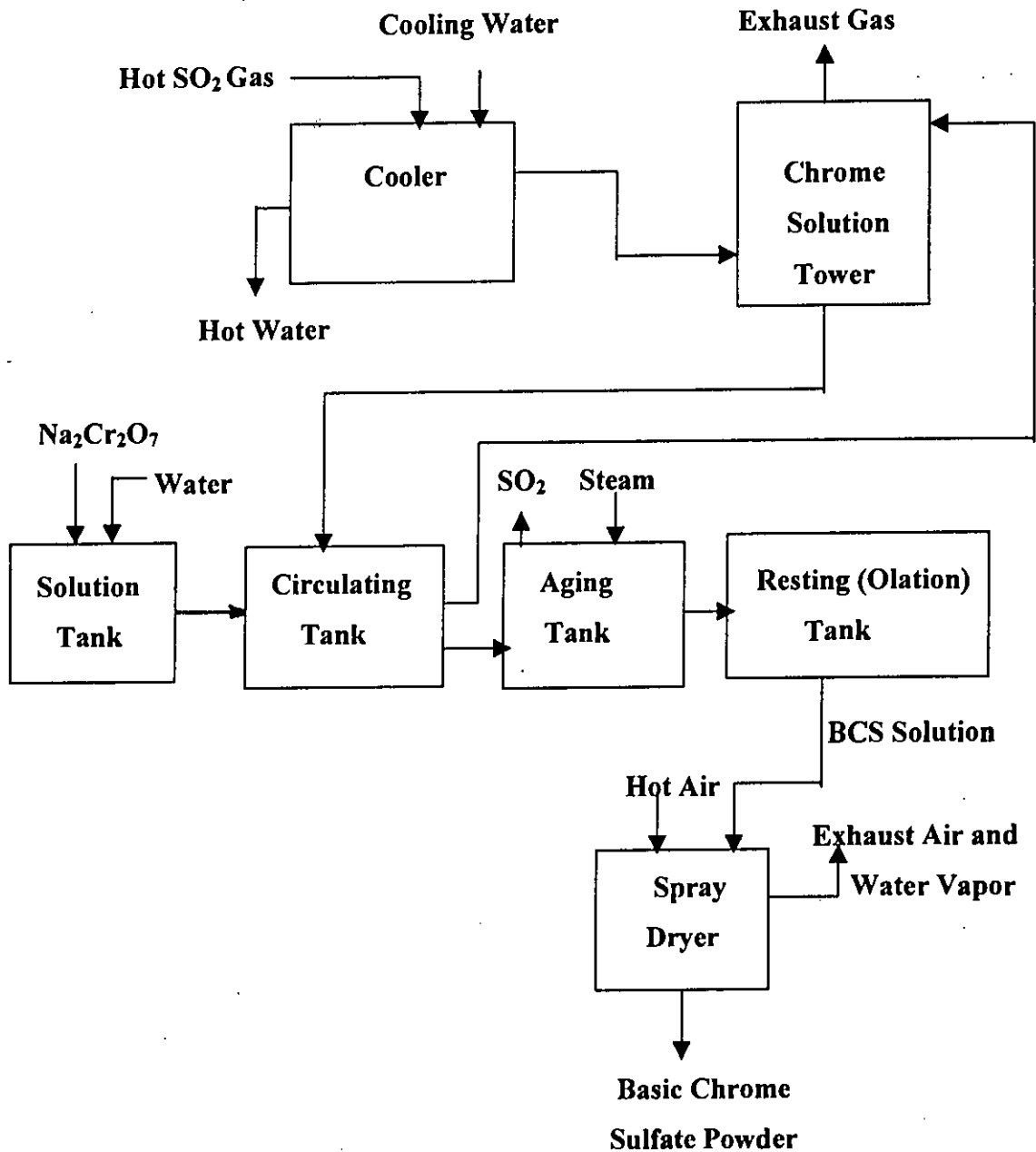


Fig. 4 Block Diagram of Sulfur Dioxide Reduction Process using Sodium Dichromate

CHAPTER-THREE

PROCESS TECHNOLOGY

3.1 Capacity of the Plant

A large quantity of Basic Chrome Powder (BCP) is needed in our country for tannery industry. Most of it is imported. The plant, which is now in operation in this country, has a capacity of 10 t/day. The present study was carried out for determining the performance of this plant.

3.2 Salient Features of BCP Plant

For production of Basic Chrome Sulfate Powder from Sodium Di-chromate, the major equipment are:

1. Tank for making solution
2. Reactor for reduction
3. Aging tank
4. Resting tank
5. Spray dryer
6. Circulation tank
7. BCS solution tower

Production of Basic Chrome Sulfate Powder from Sodium Dichromate involves several steps as illustrated in Fig. 5.

Production of SO₂ Gas

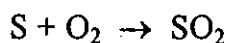
Step-1: Sulfur melting

The existing Sulfuric Acid Plant at WATA Chemicals Ltd. supplies the molten sulfur to the sulfur dioxide generation plant.

Step-2: Production of SO₂

Molten sulfur from existing sulfur melting pit is pumped by a variable speed gear pump into the sulfur burner. The clean sulfur is sprayed into the sulfur burner where it burns in the presence of air to form sulfur dioxide. The quantities of air and sulfur are adjusted so that the burner gases contain about 8.5% sulfur dioxide. For starting up, when the burner will be cold, gas firing is done to raise the temperature of the burner to the required level. Once the plant is put on sulfur, gas firing is not required since the burning of sulfur is self sustaining and results in products of combustion at a high temperature.

The combustion reaction takes place between oxygen of air and sulfur in the sulfur burner as



Step-3: Cooling of SO₂ gas

As this temperature is too high for further processing, the gases are cooled in an atmospheric cooler and sent into the hot gas filter. In the filter any dust suspension in the gases is removed which will, otherwise, get settled in the packed bed of the reduction tower and the downstream units increasing the pressure drop and impairing the efficiency.

Production of 45% Basic Chrome Sulfate Solution

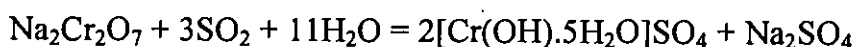
Step-4: Preparation of dichromate solution

Sodium dichromate solution of about 45% concentration is prepared in solution tank. The process water, comes from the battery limit, is transmitted into the solution tank and mixed with the sodium dichromate of fixed quantity. Then, the prepared solution is transferred to the BCS circulation tank by the solution transfer pump.

Step-5: Reduction of sodium dichromate solution

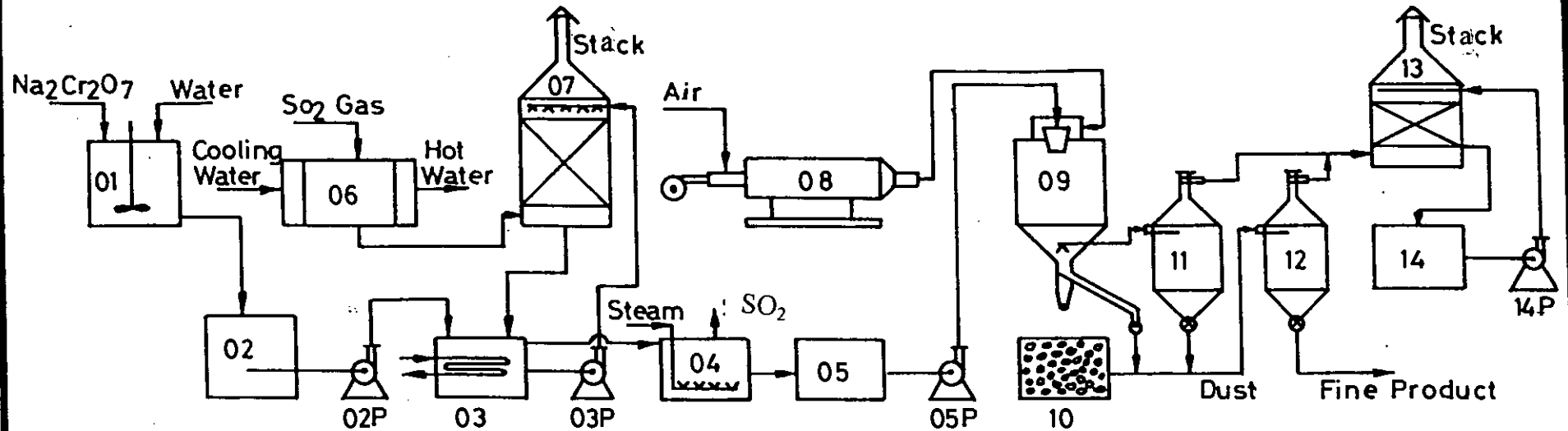
Sulfur dioxide gas emerging from the hot gas filter at 420⁰C is further cooled down by water in SO₂ gas cooler. The dichromate solution which comes from the circulation tank is reduced by sulfur dioxide gas in a closed circuit operated by counter-current circulation in a packed bed tower (chrome solution tower) at 50⁰C to 60⁰C. The recirculating liquid gradually changes color from golden yellow to greenish yellow and finally attains bottle green coloration as a thick liquid of 40-48⁰Be.

The reaction taking place between sodium dichromate and sulfur dioxide gas in the reduction tower is as follows:



Step-6: Aging and pre-heating of BCS solution

The reduced solution which comes from circulation tank goes into the aging tank where undesirable impurities like phosgenos formed during the reduction process is removed by bubbling steam through the BCS solution which causes proper aging of the liquor. As such excess sulfur dioxide is removed.



01 : Reaction Tank
 02 : Dichromate Solution Tank
 02P: Dichromate Pump
 03 : Circulation Tank
 03P: Circulation Pump
 04 : Aging Tank With
 Steam Sparger
 05 : Resting (Olation) Tank
 05P: BCS Solution Pump

06 : SO₂ Gas Cooler
 07 : Chrome Reduction Tower
 08 : Air Heater
 09 : Spray Dryer
 10 : Basic Chrome Sulfate
 Powder Storage Tank
 11 : Main Cyclone
 12 : Conveying Cyclone
 13 : Scrubber

14 : Soda Ash Circulation Tank
 14P: Soda Ash Circulation Pump

**FIG. 5 PROCESS FLOW DIAGRAM FOR
 BASIC CHROME SULFATE
 PRODUCTION FROM SODIUM
 DICHROMATE**

Step-7: Resting (Olation)

After aging the slurry is passed into the resting tank for olation. In this section basicity and unreduced Cr^{+6} to be checked and solution is pre-heated up to 80°C to 90°C . This pre-heated solution is ready for spray drying.

Drying of Basic Chrome Sulfate Solution

Step-8: Process description on spray dryer:

The process is based on the spray drying system, where a liquid is sprayed in a drying chamber by a centrifugal atomizer.

The fresh ambient air heated in a direct fired hot air generator comes in contact with the feed spray and in a co-current passage down the chamber gets dried to the required level of dryness. The dry powder is discharged through rotary air lock valve. The fine powder is conveyed along with exhaust air to a high efficiency cyclone separator and is discharged through a rotary air lock valve. The exhaust gases are then treated for fine recovery in a direct contact wet scrubber before venting to the atmosphere through chimney. The spray drying plant is operated through a instrument panel complete with imitative indication alarm and instrumentation for automatic control. Material discharged from the cyclone is cooled and conveyed pneumatically to a product bagging cyclone.

CHAPTER-FOUR

EXPERIMENTAL PROCEDURES

Major Tests for BCP Product

The product has to be analyzed since demand depends on product quality, for this the following tests are important:

- 4.1 Basicity and Chromium Oxide Content
- 4.2 pH
- 4.3 Sodium Sulfate Content
- 4.4 Unreduced Chromium Content

4.1 Basicity and Chromium Oxide content

At first, a clean and dry weighing bottle is taken and weighed. Let us consider it is W_1 gms. Then about 15 gms of powder is taken as a sample and weighed. Say it is W_2 gms. It is transferred to a beaker with water and heated gently to dissolve then it is transferred and cooled. Water is added with this volume making 500 ml solution in a volumetric flask, and then it is cooled. From volumetric flask, 25 ml is taken to a 500 ml conical flask (part1) and 5 ml to another solution flask (part 2).

Part 1 - % Cr_2O_3 content determination

A funnel is put into 500 ml conical flask. And 2(N) NaOH solution is added in excess to dissolve the precipitate which appeared initially. 15 ml of 30% Hydrogen Peroxide is added and allowed in rest for 5 minutes for completing reaction then it is boiled gently till the excess Hydrogen Peroxide is removed and again cooled. It is transferred to a 250 ml volumetric flask and made up the volume up to the mark. 5 ml is taken into a Iodometric flask. And 7 ml analytic reagents of concentrated hydrochloric acid and 2 ml Potassium Iodide solution (10%) are added and finally it is kept in dark for 10 mins.

The sample is titrated against standard Sodium Thio sulfate solution (0.05N) and then starch is added for change greenish color to get end point. By using the following formula, % Cr_2O_3 can be determined.

$$\% Cr_2O_3 = \{ [0.2534 \times a \times \text{strength of thio sol}^n] / [W_2 - W_1] \} \times 100$$

where, a = ml. of standard Sodium thio sulfate added $\times 10$

Part 2 - % Basicity determination

100 ml water and 2-3 ml of phenolphthalein indicator are added in 5 ml solution flask and then titrated against standard NaOH solution (0.1N). Pink color appears. This

solution is stirred continuously with glass rod and boiled and then cooled when the precipitate settle, again standard NaOH solution is added till the pink color appear. By using the following formula, %basicity can be determined:

$$\% \text{ basicity} = \{[a-b] / a\} \times 100 \%$$

where,

a = ml. of standard sodium thio sulfate added \times 10

b = [ml. of standard caustic added \times strength of caustic Soda] / [strength of sodium thio Sulfate solⁿ]

4.2 pH

10 gm powder is taken to a 100 ml beaker and some water is added. It is heated for obtaining clear solution and then cooled and the volume is made up to the mark. pH of test sample is measured directly by a digital pH meter

4.3 Sodium Sulfate Content

From the part2, the contents of solution flask is filtered to a 1000 ml volumetric flask and washed thoroughly. The volume is made up to the mark. 200 ml solution is taken to a 500 ml beaker and add 15 ml concentration of HCl. Boil it, then add 50 ml 10% hot Barium chloride solution. Allow to settle for 2 hours. Filter it in Gooch Crucible. Dry it at 110°C for 2 hours.

By using the following formula, % free Sulfate as Na₂SO₄ can be determined:

a) % Total Sulfate as Na₂SO₄

$$=[\text{difference in wt. of Gooch Crucible} \times 5 \times 10 \times 60.86] / [\text{wt. of powder taken}]$$

% Sulfate combined with Chromium

$$=[0.071 \times 10 \times 100 \text{ ml. of standard Caustic added} \times \text{strength of Caustic Soda}] / \text{wt. of powder taken.}$$

Hence, % Free Sulfate as Na₂SO₄ = [% total Sulfate] - [% combined with Chromium Sulfate].

4.4 Unreduced Chromium

5 mg sample powder is taken and it is diluted 6 to 7 times with water. This solution is heated until clear and then cooled. Ammonium hydroxide solution (1:10) is added till smell of ammonia persists. As a result precipitation occurs and then the solution is cooled. Fresh solution is collected by filtering and 2(N) Sulfuric acid, 10% potassium iodide solution and 5 to 6 drops of starch solution are added. It is kept in rest for 40 mins. If the solution is colorless then there is no unreduced chromium (Cr⁺⁶), otherwise, it shows pink color.

CHAPTER-FIVE

RESULTS AND DISCUSSIONS

The results, determined at the laboratory for the Basic Chrome Sulfate, are summarized in table 3.

Table 3 Experimental Values for Basic Chrome Sulfate

Places	pH	Basicity	Cr ₂ O ₃	Na ₂ SO ₄	Unreduced chromium
Lab. in WATA Chemicals	2.8	37.04%	24.92%	-	No
Chemistry Lab. in BUET	2.9	34.5%	24.1%	24.5%	No

The experimental value of pH was found as 2.8 at the WATA Chemicals laboratory and 2.9 at the chemistry laboratory in the BUET. But the actual value of pH of basic chrome sulfate is approximately 2.8. This slight variation occurred due to the digital pH meter reading. If the pH value of the chrome tanning liquor increases, the molecule of the chromium salt becomes large, thereby penetration rate of the tan liquor into the skin will be reduced. Chrome liquor with a high pH value may therefore cause over tannage of the outer layer of the skin resulting in drawn of the grain. The pH value of chrome liquor changes upon the addition of acid or alkali, and a function of aging, heating of the liquor or upon the addition of natural salts. Actually acid lowers the pH value and alkali increases the pH value. When free acid is present in the chrome liquor, the liquor penetrates the skin more easily than the basic chrome salt. The chrome liquor will become more basic and more colloidal due to hydrolysis. At a pH of 2.8 and basicity of 33%, the basic chrome sulfate is soluble and will make the leather to resist heat, water and remain soft and flexible upon drying.

The basicity of basic chrome sulfate was found as 37.04% at WATA Chemicals laboratory and 34.5% at the chemistry laboratory of BUET that is shown in Table 3. Since the same sample and same procedure were used to carry out experiments, there is variation between two results because of experimental error. But 33% basicity of basic chrome sulfate is desirable which makes the leather comfortable to use. If the basicity is increased the number of OH group in the chrome complex will be increased and then the size of the chrome complex also will be increased and the penetration rate into the pelt will be slowed. For practical purposes, the basicity depends upon the kind of pelt, the type of leather, the nature of process, the kind and concentration of the chrome liquor and its content of neutral salts. If the basicity is decreased, it will give an empty, hard leather. But high basicity over loads the fibers and sometimes results in a cracked grain.

From Table 3, we can see that the % Cr₂O₃ content in product is about 25% and about 4.18% system loss was found from material balance.

Na₂SO₄ content in the basic chrome sulfate is another important factor. The experimental value of Na₂SO₄ is about 24.5%, but the calculated value is 27.25% (Table 4). This discrepancy was found due to experimental error.

It can be seen from Table 3 that basic chrome sulfate contains 24.5% Na₂SO₄. The presence of Na₂SO₄ is desired from the view point of tanning. It has been observed that moderate addition of sodium sulfate to a basic chrome sulfate liquor results in the production of a full and plumpy leather (8).

Further, BCS produced in the WATA Chemicals Ltd. plant did not contain unreduced chromium, (Cr⁺⁶), Table 3.

The calculated values, found from material balances, are listed in Table 4.

Table 4 Calculated Values from Material Balances

Na ₂ SO ₄	SO ₃	H ₂ O	OH
27.25%	26.32%	18.47% as H ₂ O	2.96%

SO₃, H₂O are found as 26.32% and 21.43% respectively from material balances. The SO₃ determined is actually present as Na₂SO₄.

The energy balance was made only around spray dryer and results are presented in Table 5.

Table 5 Summary of Heat Balance around Spray Dryer

Total Heat In Kcal/kg	Total Heat Out Kcal/kg	Total Heat Loss Kcal/kg	Total heat loss
671354.46	654419.16	~17000	2.5%

The total heat loss through spray dryer was found as 17000 kcal/kg by considering an overall heat transfer co-efficient of 1.25 kcal/m²-°C-hr. This loss is 2.5% of the total heat input.

CHAPTER-SIX

CONCLUSIONS

Since most of the chemical plants are hazardous for their waste discharge in the environment, from the engineering point of view, it is important to study the performance of a chemical plant.

The following conclusions can be made from the performance study of the BCS plant of WATA Chemicals Ltd.:

- 1) In our country, sodium dichromate is used as a raw material for BCS production. In this type process the costs of equipment and manpower are less and the manufacturing procedure easier compared to the process based on chrome ore.
- 2) The range of pH value of BCS may be 2.8- 3.6, and common value is 2.8.
- 3) The range of basicity of BCS may be 33-58.3%. But the most common value is 33%.
- 4) The total heat loss with respect to heat input in spray dryer is about 2.5% by considering overall heat transfer co-efficient of $1.25 \text{ kcal/m}^2\text{-}^\circ\text{C-hr}$.
- 5) Results of product composition obtained from the overall material balance of the plant are in good agreement with experimentally determined values.
- 6) Results were found to be satisfactory from the viewpoint of commercial use of BCS for tanning.

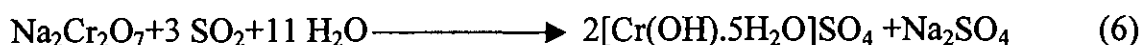
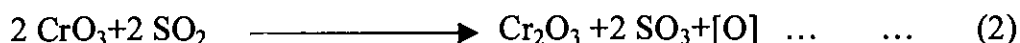
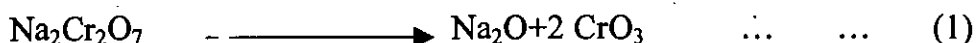
REFERENCES

1. Farduz Zaman, Tannery Industries of Bangladesh, Bangladesh Business Review, Vol.1, No.2, July-August 1998.
2. Kirk- Othmer, 'Encyclopedia of Chemical Technology', 3rd edition, volume-6, John Wiley and Sons, New York, 1979 and Volume-14, 1982.
3. ESCASP, 'Industrial Pollution Control Guide-lines', Bangkok, 1982.
4. Shilpa Prokoushali, 'Pre-investment Study on Sodium Dichromate for Bangladesh Chemical Industries Corporation', June, 1992.
5. Meketta, John J. 'Encyclopedia of Chemical Processing and Design', Volume-8, Marcel DEKKER, Inc.,1979.
6. Masters, K., 'Spray Drying Handbook', Fourth edition, George London, 1985.
7. Venkaswartzu D, 'Chemitech-1: Manual of Chemical Technology', Volume-1, 1st edition, S.chand and company Ltd., New Delhi, 1975.
8. Sarkar, K.T, 'Theory and Practice of Leather Manufacture', 1st edition, India, 1965.
9. Sashanka Shekhar Dutta, 'An Introduction to the Principles of Leather Manufacture', Indian Leather Technologist Association, Calcutta, India.
10. WATA Chemicals Ltd. (Private Communication).

APPENDICES

A. Reaction Mechanism of Basic Chrome Sulfate Production

The reactions taking place during the production of basic chrome sulfate from sodium dichromate are illustrated below :



B. Overall Material Balance

The composition of basic chrome sulfate in terms of Cr_2O_3 , Na_2SO_4 , SO_3 , H_2O and OH group is calculated from the overall material balance using the above reactions.

The molecular weight of different compounds used for material balance are given in the following table:

Compounds	Molecular Weight
$[\text{Cr}(\text{OH}) \cdot 5 \text{H}_2\text{O}] \text{SO}_4$	255
$\text{Na}_2\text{Cr}_2\text{O}_7$	262
Cr_2O_3	152
SO_3	80
SO_2	64
Na_2SO_4	142
O_2	32
$\text{Cr}(\text{OH}) \text{SO}_4$	165
Na_2O	62
H_2O	18

Basis: 1000kg/hr Na₂Cr₂O₇ of 99% purity

Calculation of Process Loss of Chromium as Cr₂O₃

From plant performance it is known that 1000Kg Na₂Cr₂O₇ is used for production of 2200Kg basic chrome sulfate powder (BCP).

One ton Na₂Cr₂O₇ contains

$$=1000\text{Kg Na}_2\text{Cr}_2\text{O}_7 \times (1\text{KmolNa}_2\text{Cr}_2\text{O}_7/262\text{Kg Na}_2\text{Cr}_2\text{O}_7) \times (152\text{KgCr}_2\text{O}_3 /1\text{Kmol Cr}_2\text{O}_3) \times 0.99 = 574.35 \text{ Kg Cr}_2\text{O}_3$$

Product (Laboratory) analysis:

$$\text{Cr}_2\text{O}_3 = 25\% \text{ in product B.C.P.}$$

$$\begin{aligned} \text{total Cr}_2\text{O}_3 \text{ in product} &= 2200 \times 0.25 \\ &= 550\text{Kg} \end{aligned}$$

$$\begin{aligned} \text{process loss} &= \text{supplied-yield} \\ &= (574.35 - 550) \text{ Kg Cr}_2\text{O}_3 \\ &= 24.35 \text{ Kg Cr}_2\text{O}_3 \end{aligned}$$

$$\begin{aligned} \% \text{ process loss} &= 24.35 / 574.35 \times 100 \% \\ &= 4.24 \% \end{aligned}$$

Calculation of Na₂SO₄ Content

One ton Na₂Cr₂O₇ can produce =

$$\begin{aligned} & \frac{[\text{molecular wt. of Na}_2\text{SO}_4 \times \text{wt. of Na}_2\text{Cr}_2\text{O}_7] \times \text{yield \%}}{[\text{molecular wt. of Na}_2\text{Cr}_2\text{O}_7]} \\ &= \{[142/(262 \times .99)] \times 1000 \times (1-0.0424)\} \text{ Kg Na}_2\text{Cr}_2\text{O}_7 \\ &= 524.25 \text{ Kg Na}_2\text{SO}_4 \end{aligned}$$

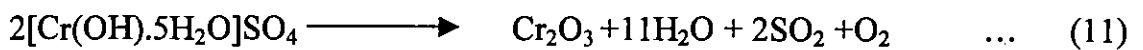
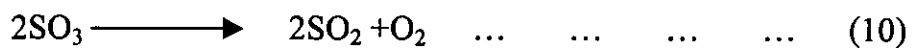
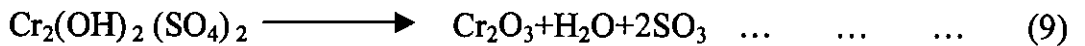
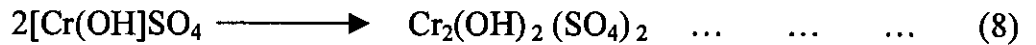
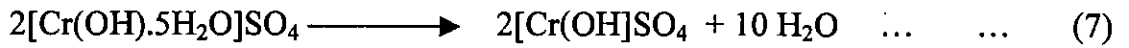
Na₂SO₄ added: 75 Kg(excess)

Total Na₂SO₄ produced = 524.25 + 75 = 599.25 Kg

$$\begin{aligned} \% \text{ Na}_2\text{SO}_4 \text{ in BCP} &= \{[\text{total wt. of Na}_2\text{SO}_4]/[\text{production of BCP}]\} \times 100\% \\ &= [599.25 / 2200] \times 100\% \\ &= 27.24\% \end{aligned}$$

Determination of SO₂ used on the basis of Cr₂O₃ weight

For material balance purpose BCS, 2[Cr(OH).5H₂O]SO₄ may be decomposed in the following way:



Basis: 550 Kg Cr₂O₃ in 2200 Kg BCP

SO₂ used for production of one mole of Cr₂(OH)₂(SO₄)₂ according to reactions (9) and (10)

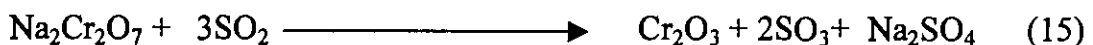
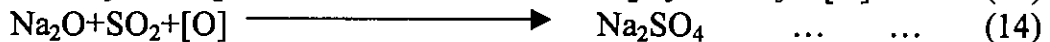
$$\begin{aligned} &= 2[\text{molecular wt. of SO}_2 \times \text{wt. of Cr}_2\text{O}_3 / \text{molecular wt. of Cr}_2\text{O}_3] \\ &= 2 \times [64 \times 550 / 152] \\ &= 463.16 \text{ Kg SO}_2 \end{aligned}$$

$$\begin{aligned} \text{SO}_3 &= [\text{molecular wt. of SO}_3 \times \text{wt. of SO}_2 / \text{molecular wt. of SO}_2] \\ &= [80 \times 463.16 / 64] \text{ Kg} \\ &= 578.95 \text{ Kg} \end{aligned}$$

$$\begin{aligned} \% \text{SO}_3 &= [578.95 / 2200] \times 100\% \\ &= 26.32\% \end{aligned}$$

SO₂ required for Na₂SO₄ Production

The production of SO₂ from Na₂Cr₂O₇ and 2SO₃ can be summarized as the following way:



Na₂O in sodium dichromate according to reaction (12)

$$\begin{aligned} &= [\text{mol. wt. of Na}_2\text{O} \times \text{wt. of Na}_2\text{Cr}_2\text{O}_7 / \text{mol. wt. of Na}_2\text{Cr}_2\text{O}_7] \times 0.99 \\ &= [62 \times 1000 / 262 \times 0.99] \text{ Kg} \\ &= 234.27 \text{ Kg} \end{aligned}$$

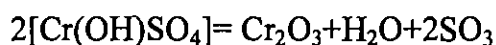
$$\begin{aligned}
 \text{SO}_2 \text{ required to convert sodium oxide into Na}_2\text{SO}_4 \text{ according to reaction (14)} \\
 &= [\text{mol. wt. of SO}_2 \times \text{wt. of Na}_2\text{O} / \text{mol. wt. of Na}_2\text{O}] \\
 &= 64 \times 234.27 / 62 \text{ Kg} \\
 &= 242 \text{ Kg}
 \end{aligned}$$

$$\begin{aligned}
 \text{Total SO}_2 \text{ required} &= \text{SO}_2 \text{ for Cr(OH)SO}_4 + \text{SO}_2 \text{ for Na}_2\text{SO}_4 \\
 &= (463.16 + 242) \text{ Kg} \\
 &= 705.16 \text{ Kg}
 \end{aligned}$$

Water Determination as Combined and OH group

$$\begin{aligned}
 \text{Water for OH and H}_2\text{O in Cr(OH)SO}_4 \cdot 5\text{H}_2\text{O} \\
 &= \text{total production} - \text{wt. of Cr}_2\text{O}_3 - \text{wt. of Na}_2\text{SO}_4 - \text{Wt. of SO}_3 \text{ in Cr(OH)SO}_4 \\
 &= 2200 - (550 + 599.25 + 578.95) \\
 &= 471.8 \text{ Kg of water (both OH and combined water)}
 \end{aligned}$$

Combination of reactions (8) and (9) results



$$\begin{aligned}
 \text{Water used for OH} &= [18/152] \times 550 \text{ Kg} \\
 &= 65.13 \text{ Kg}
 \end{aligned}$$

$$\begin{aligned}
 \text{H}_2\text{O for OH} &= 65.13 / 2200 \times 100\% \\
 &= 2.96\%
 \end{aligned}$$

$$\begin{aligned}
 \text{Water used as combined water/free water} \\
 &= (471.8 - 65.13) \text{ Kg} \\
 &= 406.67 \text{ Kg}
 \end{aligned}$$

$$\begin{aligned}
 \text{Water in BCP} &= 406.67 / 2200 \times 100\% \\
 &= 18.48\%
 \end{aligned}$$

Summary of results of product analysis

Cr ₂ O ₃	= 25%
Na ₂ SO ₄	= 27.24%
SO ₃	= 26.32%
H ₂ O	= 18.48
OH	= 2.96%
<hr/>	
Total	= 100%

C. Sample Calculation of Laboratory Tests

Basicity

Formula for basicity calculation:

$$\% \text{ basicity} = \{[a-b] / a\} \times 100 \%$$

where,

$$a = \text{ml. of standard Sodium thio sulfate added} \times 10$$

$$b = [\text{ml. of standard Caustic added} \times \text{strength of Caustic Soda}] / [\text{strength of Sodium thio Sulfate solution}]$$

Initial burette reading of standard Sodium thio sulfate solution = 8.3 ml

Final burette reading of standard Sodium thio sulfate solution = 14.2 ml

$$a = 14.2 - 8.3 \times 5 \times 10 = 295 \text{ ml}$$

Again, initial burette reading of standard Caustic solution = 6.2 ml

Final burette reading of standard Caustic solution = 24.3 ml

Strength of Caustic Soda = 0.10264384892(N)

Strength of standard Sodium thio sulfate solution = 0.05001552763(N)

$$b = \{(24.3 - 6.2) \times 5\} \times 0.10264384892 / 0.05001552763 \\ = 185.727 \text{ ml}$$

$$\% \text{ basicity} = \{[a-b] / a\} \times 100 \% \\ = (295 - 185.727) / 295 \times 100 \% \\ = 37.041 \%$$

% Cr₂O₃

formula for % Cr₂O₃ calculation:

$$\% \text{ Cr}_2\text{O}_3 = \{[0.2534 \times a \times \text{strength of thio sol}^n] / [W_2 - W_1]\} \times 100\% \\ = \{[0.2534 \times 295 \times 0.05001552763] / [15]\} \times 100\% \\ = 24.92\%$$

pH

Powder taken=10 gm in a 100 ml beaker and made up the volume up to 100 ml. This solution is heated and stirred so that colloidal particles are dissolved clearly in that solution. pH is measured directly by digital pH meter and recorded the pH as 2.8.

% Free Sulfate as Na_2SO_4

Powder taken = 15 gm.

weight of empty Gooch Crucible = 41.956 gm.

Weight of Gooch Crucible with sample = 42.118 gm.

Difference in wt. of Gooch Crucible = 0.162 gm.

% total Sulfate as Na_2SO_4

$$\begin{aligned} &= \{(\text{difference in wt. of Gooch Crucible} \times 5 \times 10 \times 0.6086) / (\text{wt. of powder taken})\} \times 100\% \\ &= (0.162 \times 5 \times 10 \times 0.6086 / 15) \times 100\% \\ &= 32.86\% \end{aligned}$$

Standard Caustic Soda added = final reading - initial reading

$$= 23.77 - 5.56 = 18.209 \text{ ml.}$$

Strength of Caustic Soda = 0.1 (N)

% Sulfate combined with chromium

$$\begin{aligned} &= [(0.071 \times 10 \times \text{ml. of standard caustic soda added} \times \text{strength of caustic soda}) / \\ &\quad (\text{wt. of powder taken})] \times 100\% \\ &= 0.071 \times 10 \times 18.209 \times 0.1 / 15 \times 100\% \\ &= 8.56\% \end{aligned}$$

% free Sulfate as $\text{Na}_2\text{SO}_4 = (32.86 - 8.56)\%$

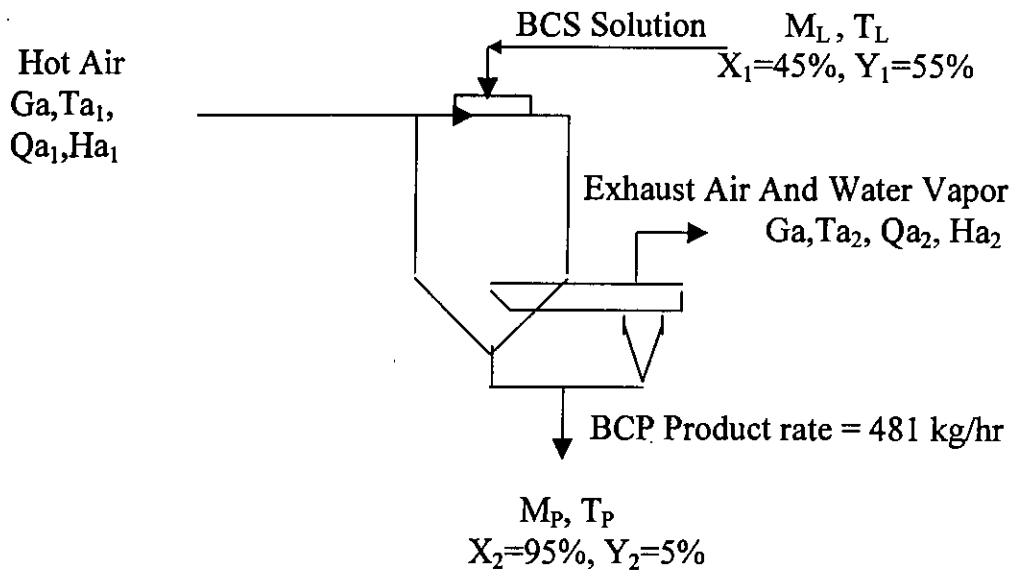
$$= 24.3\%$$

D. Mass and Heat Balances around Spray Dryer

45% BCS solution at room temperature is dried using hot air (250°C) to obtain BCS powder with 5% moisture.

a. Mass Balance

Evaporation rate of water from the BCS solution fed to the spray dryer is calculated by mass balance. Then the evaporation rate is compared with the specified values for the spray dryer.



M_L = Flow rate of Liquid BCS into spryer dryer

M_p = Flow rate of BCP product

G_a = Flow rate of air into spray dryer

Q_{a1} = Enthalpy (Heat) of inlet dry air

Q_{a2} = Enthalpy of outlet air

H_{a1} = Absolute humidity of inlet air

H_{a2} = Absolute humidity of outlet air

T_L = Temperature of BCS solution = 20°C

T_p = Temperature of BCP product = 80°C

T_{a1} = Temperature of inlet air = 250°C

T_{a2} = Temperature of outlet air = 100°C

X_1 = Percent of solid in feed to dryer = 45%

X_2 = Percent solid in product from dryer = 95%

Y_1 = Percent water in feed to dryer = 55%

Y_2 = Percent moisture in product from dryer = 5%

Basis: 481 Kg/hr BCP production

$$\begin{aligned}\text{Feed rate to dryer, } M_L &= M_P \times X_2 / X_1 \text{ kg/hr} \\ &= (481 \times 95 / 100) / [45 / 100] \text{ kg/hr} \\ &= 1015.44 \text{ kg/hr}\end{aligned}$$

$$\begin{aligned}\text{Water entering in feed, } W_{s1} &= Y_1 / X_1 \\ &= 55 / 45 \\ &= 1.22 \text{ kg/kg dry solid}\end{aligned}$$

$$\begin{aligned}\text{Moisture in dried product, } W_{s2} &= Y_2 / X_2 \\ &= 5 / 95 \\ &= 0.053 \text{ kg/kg dry solid.}\end{aligned}$$

$$\begin{aligned}\text{Dry solids in product, } M_s &= M_P \times X_2 \text{ kg/hr} \\ &= 481 \times 95 / 100 \text{ kg/hr} \\ &= 456.95 \text{ kg/hr}\end{aligned}$$

Moisture Balance

Basis : Dry solids in product = 456.95 kg/hr

$$\begin{aligned}\text{Water entering in feed, } M_{mL} &= M_s \times W_{s1} \\ &= 456.95 \times 1.22 \text{ kg/hr} \\ &= 557.48 \text{ kg/hr}\end{aligned}$$

$$\begin{aligned}\text{Moisture leaving in product, } M_{mp} &= M_s \times W_{s2} \\ &= 456.95 \times 0.053 \text{ kg/hr} \\ &= 24.22 \text{ kg/hr}\end{aligned}$$

$$\begin{aligned}\text{Water evaporated, } M_{mE} &= M_s \times \{W_{s1} - W_{s2}\} \\ &= 456.95 \times (1.22 - 0.053) \text{ kg/hr} \\ &= 533.26 \text{ kg/hr}\end{aligned}$$

Summary of Results

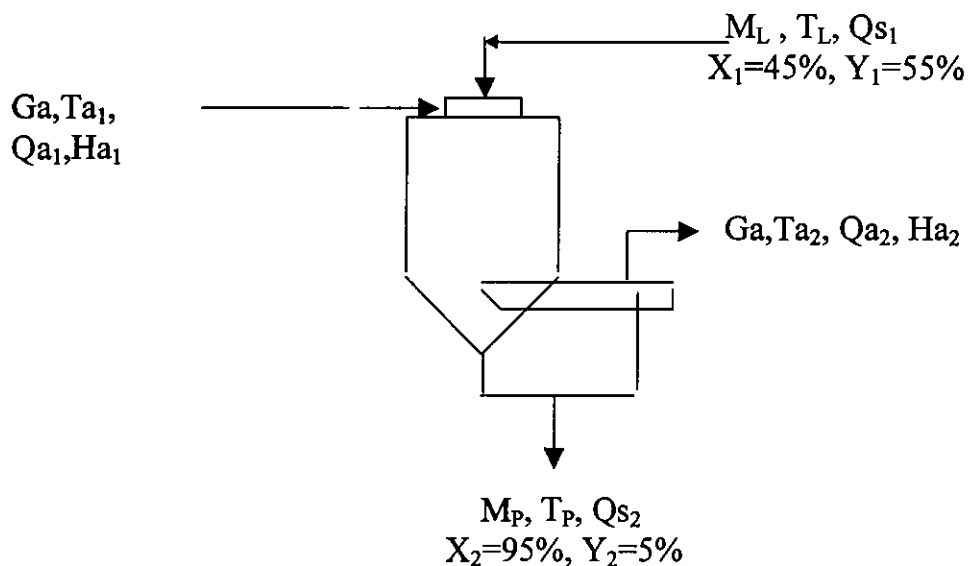
Evaporation rate: 533.26 kg/hr

Designed evaporation rate: 542 kg/hr

Guaranteed evaporation rate: 515 kg/hr

b. Heat Balance

Energy balance around spray dryer was carried out employing the procedure outlined by Masters (6). The values for the surface area of spray dryer and the overall heat transfer co-efficient for heat loss from the dryer surface to ambient air were assumed.



M_L = Flow rate of Liquid BCS into dryer = 1015.44 kg/hr

M_P = Flow rate of BCP production = 481 kg/hr

G_a = Flow rate of dry air

Q_{a1} = Enthalpy(Heat) of inlet air

Q_{a2} = Enthalpy of outlet air

H_{a1} = Absolute humidity of inlet air = 0.005 kgH₂O/kgdry air (from humidity chart)

H_{a2} = Absolute humidity of outlet air

Q_{S1} = Enthalpy of feed entering dryer

Q_{S2} = Enthalpy of product leaving dryer

X_1 = Percent solid in feed to dryer = 45%

X_2 = Percent solid in product from dryer = 95%

Y_1 = Percent water in feed to dryer = 55%

Y_2 = Percent moisture in product from dryer = 5%

C_{DS} = Heat capacity of dried solids = 0.4 kcal/kg.⁰C

C_W = Heat capacity of liquid (moisture) = 1.0 kcal/kg.⁰C

T_r = Reference temperature = 0⁰C

T_L = Temperature of BCS solution = 20⁰C

T_P = Temperature of BCP product = 80⁰C

T_{a1} = Temperature of inlet air = 250⁰C

T_{a2} = Temperature of outlet air = 100⁰C

A = Surface area of the drying chamber (assumed) = 170 m²

U = Overall Heat transfer co-efficient = 1.25 kcal / m²·⁰C-hr

Heat loss, $Q_L = (U A \Delta T)$ kcal/kg

$$= 1.25 \times 170 \times (100-20) \text{ kcal/kg}$$

$$= 17000 \text{ kcal/kg}$$

$$\begin{aligned} \text{Humid heat, } C_s &= C_{PD} + C_{PV} H_a \\ &= (0.24 + 0.46 H_a) \text{ kcal/kg dry air} \quad \dots\dots(1) \end{aligned}$$

Here, C_{PD} = Specific heat of dry air and C_{PV} = Specific heat of water vapor
 The total enthalpy (heat) of a mixture of air and its water vapor for unit mass, the sum of the air and vapor enthalpy, is, $Q_a = [C_s \Delta T + \lambda H_a]$ kcal/kg
 $= (0.24 + 0.46 H_a) (T_a - T_r) + \lambda H_a \dots\dots(2)$

Where, ΔT = Temperature difference respect to reference temperature

And λ = Latent heat of vaporization

From equⁿ (2), we get

$$\begin{aligned} \text{Enthalpy of inlet air, } Q_{a1} &= [(0.24 + 0.46 H_{a1})(T_{a1} - T_r) + \lambda H_{a1} \\ &= [(0.24 + 0.46 \times 0.005)(250 - 0) + 597 \times 0.005] \text{ kcal/kg} \\ &= 60.575 \text{ kcal/kg} \end{aligned}$$

$$\begin{aligned} \text{Enthalpy of outlet air, } Q_{a2} &= (0.24 + 0.46 H_{a2})(100 - 0) + 597 \times H_{a2} \text{ kcal/kg} \\ &= 24 + 46 H_{a2} + 597 H_{a2} \\ &= 24 + 643 H_{a2} \quad \dots\dots\dots(3) \end{aligned}$$

$$\begin{aligned} \text{Enthalpy of feed entering dryer, } Q_{s1} &= \text{Enthalpy of dry solid} + \text{Enthalpy of Water} \\ &= C_{DS} \Delta T + W_{s1} C_W \Delta T \\ &= 0.4 \times (20 - 0) + 1.22 \times 1 \times (20 - 0) \\ &= 32.40 \text{ kcal/kg} \end{aligned}$$

$$\begin{aligned} \text{Enthalpy of dried product leaving dryer, } Q_{s2} &= C_{DS} \Delta T + W_{s2} C_W \Delta T \\ &= 0.4 \times (80 - 0) + 0.053 \times 1.0 \times (80 - 0) \\ &= 36.24 \text{ kcal/kg} \end{aligned}$$

Water balance for no product accumulation in the chamber,

$$\text{INPUT} = \text{OUTPUT}$$

$$M_s \times (W_{s1} - W_{s2}) = G_a \times (H_{a2} - H_{a1})$$

Values of M_s , W_{s1} and W_{s2} were calculated in mass balance. Substituting these values

$$\begin{aligned} 456.95 \times (1.22 - 0.053) &= G_a \times (H_{a2} - 0.005) \\ G_a \times (H_{a2} - 0.005) &= 533.26 \\ 533.26 / (H_{a2} - 0.005) &\dots\dots\dots(4) \end{aligned}$$

$$\text{Total enthalpy entering dryer, } Q_1 = G_a \times Q_{a1} + M_s \times Q_{s1} \quad \dots\dots\dots (5)$$

$$\text{Total enthalpy of leaving dryer, } Q_2 = G_a \times Q_{a2} + M_s \times Q_{s2} + Q_L \dots\dots\dots(6)$$

Here, heat loss, $Q_L = 17000$ kcal/hr

Since, heat in = heat out (utilized) + heat loss

$$G_a \times Q_{a1} + M_s \times Q_{s1} = G_a \times Q_{a2} + M_s \times Q_{s2} + Q_L$$

$$G_a (Q_{a1} - Q_{a2}) = M_s (Q_{s2} - Q_{s1}) + Q_L$$

$$\begin{aligned} 533.26 / (H_{a2} - 0.005) \{60.575 - (24 + 643 H_{a2})\} &= 456.95 (36.24 - 32.4) + 17000 \\ 533.26 (60.575 - 24 - 643 H_{a2}) &= (1754.688 + 17000) (H_{a2} - 0.005) \\ 19503.9845 - 342886.18 H_{a2} &= 18754.688 (H_{a2} - 0.005) \\ 19503.9845 - 342886.18 H_{a2} &= 18754.688 H_{a2} - 93.7744 \end{aligned}$$

$$18754.688 \text{ Ha}_2 + 342886.18 \text{ Ha}_2 = 19503.9845 + 93.7744$$

$$\text{Ha}_2 = 19597.7589 / 361640.868$$

$$= 0.0542 \text{ kg H}_2\text{O} / \text{kg dry air}$$

From equation (3), we get

$$\text{Qa}_2 = 24 + 643 \times \text{Ha}_2$$

$$= 24 + 643 \times 0.0542$$

$$= 58.851 \text{ kcal/kg}$$

From equation (4), we have

$$\text{Ga} = 533.26 / (0.0543 - 0.005)$$

$$= 10838.62 \text{ kg air/hr}$$

From equation (5),

$$\text{Total heat in} = \text{Ga} \times \text{Qa}_1 + \text{Ms} \times \text{Qs}_1$$

$$= 10838.62 \times 60.575 + 456.95 \times 32.4$$

$$= 671354.46 \text{ kcal/hr}$$

$$\text{Total heat out} = \text{Ga} \times \text{Qa}_2 + \text{Ms} \times \text{Qs}_2$$

$$= 10838.62 \times 58.8506 + 456.95 \times 36.24$$

$$= 654419.16 \text{ kcal/hr}$$

$$\text{Energy consumption for evaporation} = 671354.46 \text{ kcal/hr} / 533.26 \text{ kg/hr}$$

$$= 1258.96 \text{ kcal/kg of water}$$

Table 6 Summary of Heat balance around Spray Dryer

Total Heat In Kcal/kg	Total Heat Out Kcal/kg	Total Heat Loss kcal/kg	Total heat loss
671354.46	654419.16	~17000	2.5%

