SUMMER–19 EXAMINATION
Model Answer

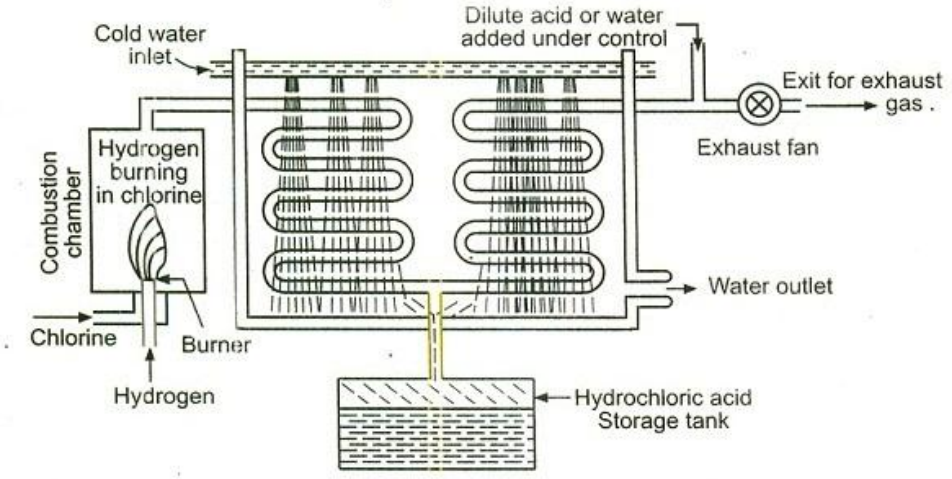
Subject Name: Technology of Inorganic Chemicals **Subject Code:** 22314

Important Instructions to examiners:

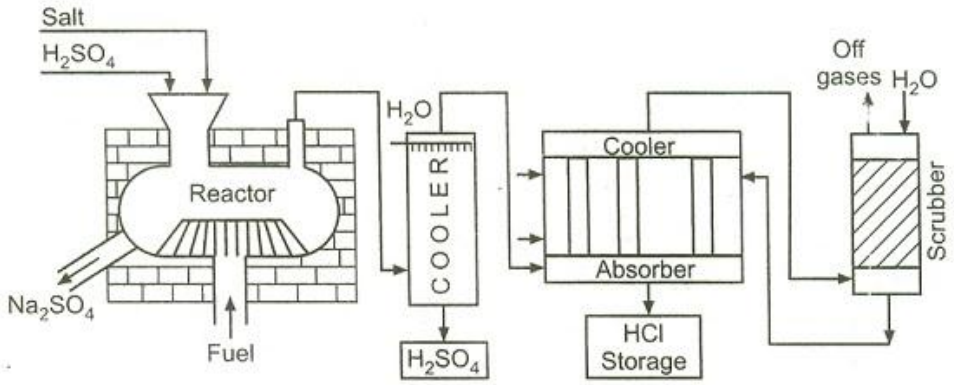
1) The answers should be examined by key words and not as word-to-word as given in the model answer scheme.
2) The model answer and the answer written by candidate may vary but the examiner may try to assess the understanding level of the candidate.
3) The language errors such as grammatical, spelling errors should not be given more Importance (Not applicable for subject English and Communication Skills.
4) While assessing figures, examiner may give credit for principal components indicated in the figure. The figures drawn by candidate and model answer may vary. The examiner may give credit for any equivalent figure drawn.
5) Credits may be given step wise for numerical problems. In some cases, the assumed constant values may vary and there may be some difference in the candidate's answers and model answer.
6) In case of some questions credit may be given by judgement on part of examiner of relevant answer based on candidate's understanding.
7) For programming language papers, credit may be given to any other program based on equivalent concept.

Q. No.	Sub Q. N.	Answer	Marking Scheme
1		**Attempt any five of the Following**	10
	a)	**Industrial Applications of water gas** • To remove carbon dioxide from fuel cells. • As a fuel gas • It is used in the Fischer-Tropsch process. • It is used to obtain pure hydrogen to synthesize ammonia. **Industrial applications of producer gas** • As fuel in coke ovens and blast furnaces • As a fuel in cement and ceramic kilns, • for mechanical power through gas engines.	1 mark each for any two from both types
	b)	**Refractory** Refractory is a material which can withstand high temperature and does not fuse. **Types** • Acid refractories • Basic Refractories • Neutral refractories	Defination 1 mark types 1 mark

	c)	**Raw materials for Sodium Carbonate** • Salt(brine) • Coal • limestone	2
	d)	**Yellow Phosphorous** Phosphorus is a chemical element with symbol P and atomic number 15 with self-imagination property when exposed to air. **Red Phosphorous** Phosphorus is a chemical element with symbol P and atomic number 15	1 1
	e)	Applications of ammonium sulphate • as a fertilizer • as a preparation for vaccines and purifying water for pharmaceuticals • as a dough conditioner • as a component in fire extinguisher powder and flame-proofing agents.	1 mark each for any two uses
	f)	**Reaction involved in manufacturing of nitric acid** $4NH_3+5O_2 = 4NO +6H_2O$ $2NO+O_2 = 2NO_2$ $3NO_2+H_2O=2HNO_3+NO$	2
	g)	**Raw materials required for ammonium nitrate** • Ammonia • Nitric Acid	1 mark each
2		**Attempt any three of the following**	**12**
	a)	**PFD for manufacturing of HCl**	4



OR

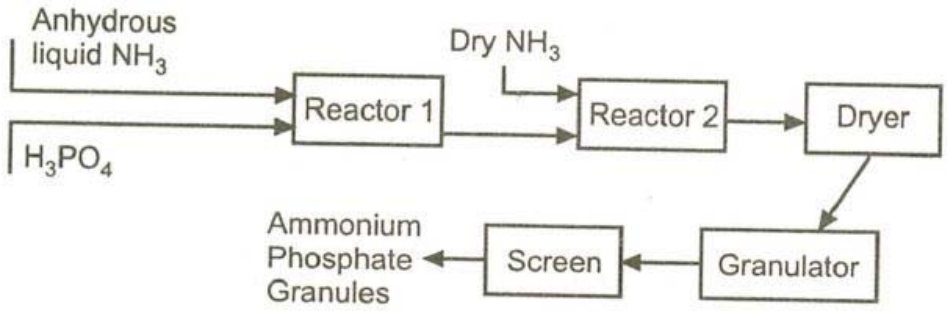


b) **Urea by Montecatini Process:** 4

Process description :

Ammonia and carbon dioxide are compressed separately and added to the high pressure autoclave which must be water cooled due to highly exothermic reaction. The average residence time in the autoclave, which is operated on a continuous basis, is 1.5 to 2 hrs. a mixture of urea, ammonium cabamate, water and unreacted NH_3 and CO_2 results.

This liquid effluent is let down to 27 atms and feed to a special flash evaporator containing gas liquid separator and condenser. unreacted NH_3, CO_2 and water as a

		solution are removed and recycled. An aqueous solution of carbamate urea is passed to the atmospheric flash drum where further decomposition of carbamate takes place. The off gases from this step can either be recycled or sent to ammonia process for making chemical fertilizers. The 80% aqueous urea solution can be used as it is or sent to a vacuum evaporator to obtained molten urea containing less than 1% water. The molten mass is them sprayed into prilling or granular solidification tower. To avoid formation of biuret in percentage > 1% , the temperature must be kept just above the melting point for processing time of 1-2 seconds in this phase of the operation.	
	c)	**Di Ammonium Phosphate** Anhydrous and dry ammonia and phosphoric acid are charged into the first reactor. About 80% neutralization is done in the first reactor. Further ammonia is added to second reactor. So conversion to the di-ammonium salt is obtained. The reaction is exothermic and hence due to heat of reaction the excess ammonia vapors are given out this are collected at the top of the tank and recharged. This cuts ammonia losses. The slurry obtained in second reactor is allowed to pass to a rotary adiabatic dryer in which moisture is reduced to less than 1%. The bed of dry particles is recycled by moving them through rotating drum granulator. The particles are screamed and dried further white crystalline solid material is obtained.  **Reaction** $NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4$ $NH_3 + NH_4H_2PO \rightarrow (NH_4)_2HPO_4$	2 1 1

	d)	**Potassium Fertilizer** **Economics** The sharp price spike during World War 1 (1914-1918) relates to the use of Chilean salt petre (potassium nitrate and sodium nitrate) in the manufacture of gunpowder (mixture of sulfur, charcoal and potassium nitrate) and to the fact that at that time the Germans exerted control of the world's potash production. Today the fertiliser industry uses more than 90-95% of produced potash, while the chemical industry uses the remainder in the manufacture of soaps and detergents, glass, ceramics, synthetic rubber and numerous industrial chemicals. The main use of potash is as a source of soluble potassium, which is one of the three primary plant nutrients; the other fertilisers are fixed and soluble phosphorus and nitrogen. Mankind's use of these three nutrients, in commercial forms, started the "Green Revolution" in agriculture in the 1950s. More than 95% of the world's potash fertiliser is today produced as muriate of potash (MOP-potassium chloride) and sylvite is the preferred ore mineral in most mines, due to relatively low processing costs. **Industries** • Ishita International, Nagpur • Kakatiya Chemicals Pvt. Ltd. AndhraPradesh • Mittal Nitrate, UP • SL Industries , Andhra Pradesh	2 2
3		**Attempt any three of the following**	**12**
	a)	**Constituent of cement and their function** **1.Lime (CaO)** Lime or calcium oxide is the most important ingredient of cement. The cement contains 60 to 67% of lime in it. It is obtained from limestone, chalk, shale etc. Adequate quantity of lime in cement is helpful to form the silicates and aluminates of calcium. If lime is added in excess quantity the cement becomes unsound as well as expansion and disintegration of cement will occur. If lime content is lower than the minimum requirement strength of cement will reduce and also setting time of cement will decrease. **2.Silica (SiO_2)** Silica or silicon dioxide is the second largest quantity of cement ingredients which is	2 marks each for any two.

about 17 to 25%. Silica can be obtained from sand, argillaceous rock etc. Sufficient quantity of silica helps for the formation of di-calcium and tri-calcium silicates which imparts strength to the cement. Excess silica in cement will increase the strength of cement but at the same time setting time of cement also increased

3.Alumina (Al_2O_3)

Alumina in cement is present in the form of aluminum oxide. The range of alumina in cement should be 3 to 8%. It is obtained from bauxite, alumina contain clay etc. Alumina imparts quick setting property to the cement. In general, high temperature is required to produce required quality of cement. But alumina when added with cement ingredients it behaves as a flux and reduces the clinkering temperature which finally weakens the cement. So, to maintain the high temperature alumina should not be used in excess quantity.

4.Iron oxide (Fe_2O_3)

Iron oxide quantity in cement is ranges from 0.5 to 6%.It can be obtained from fly ash, iron ore, scrap iron etc. The main function of iron oxide is to impart color to the cement.

At high temperatures, Iron oxide forms tricalcium aluminoferrite by reacting with aluminum and calcium. The resultant product imparts the strength and hardness properties to the cement.

5.Magnesia (MgO)

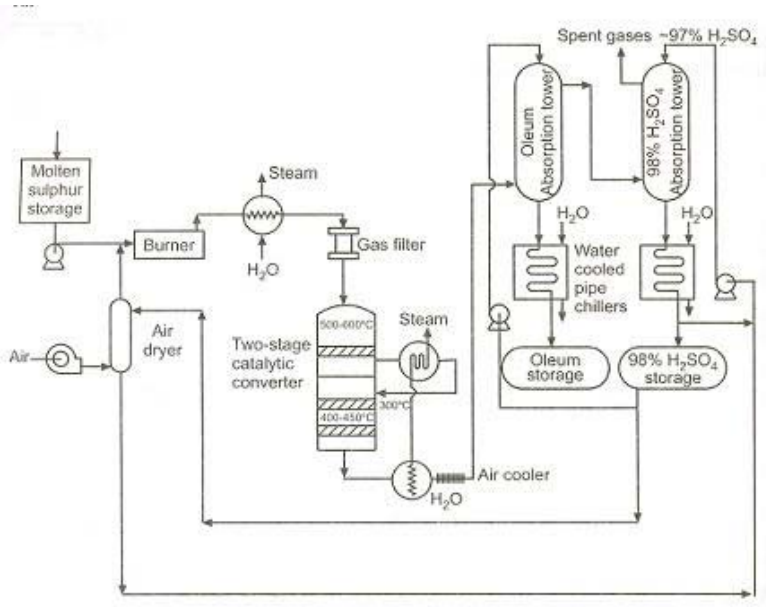
Cement contains Magnesia or Magnesium oxide in the range of 0.1 to 3%. Magnesia in cement in small quantities imparts hardness and color to the cement. If it is more than 3%, the cement becomes unsound and also strength of the cement reduces.

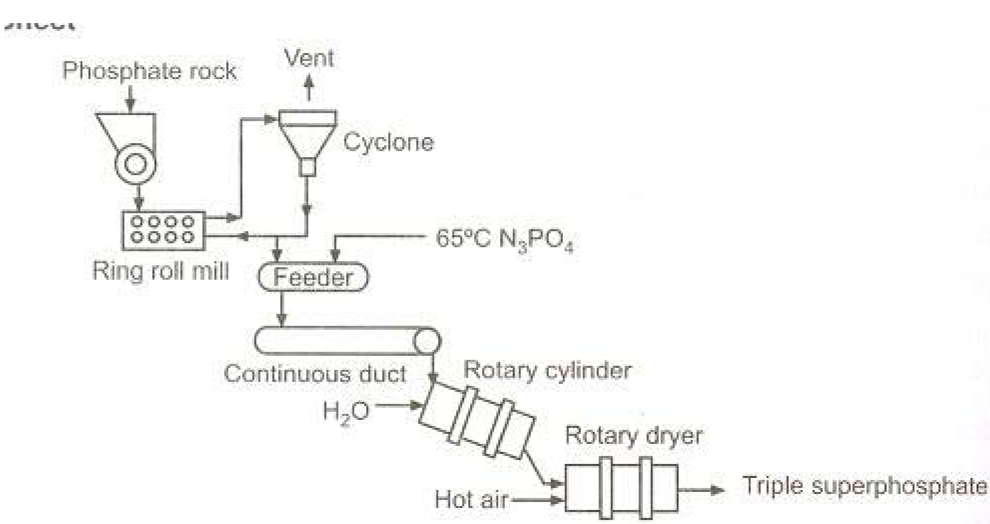
6.Calcium sulfate ($CaSO_4$)

Calcium sulfate is present in the form of gypsum in the cement. It is found together with limestone. It ranges between 1 to 3%. The function of calcium sulfate in cement is to increase the initial setting time of cement.

7. Alkalis

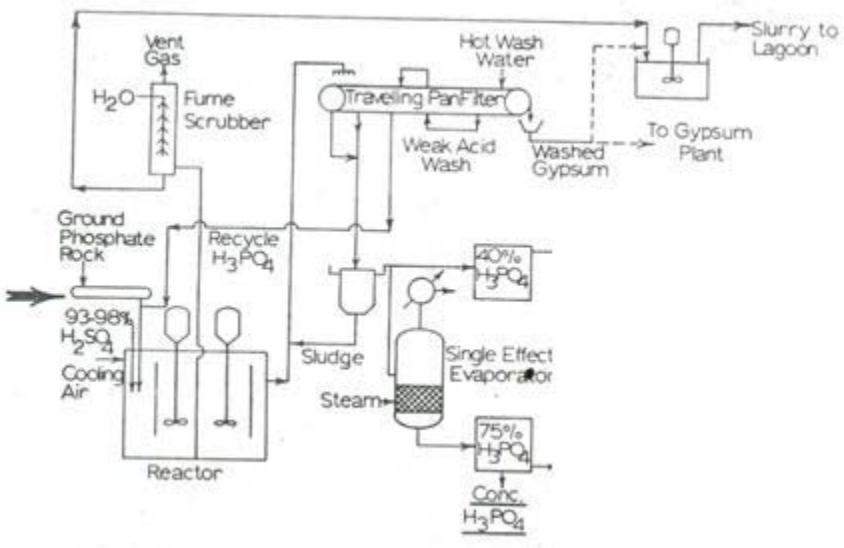
Alkalis like soda and potash are present in the cement which normally ranges from 0.1 to 1%. During manufacturing process of cement most of the alkalis are carried away by the

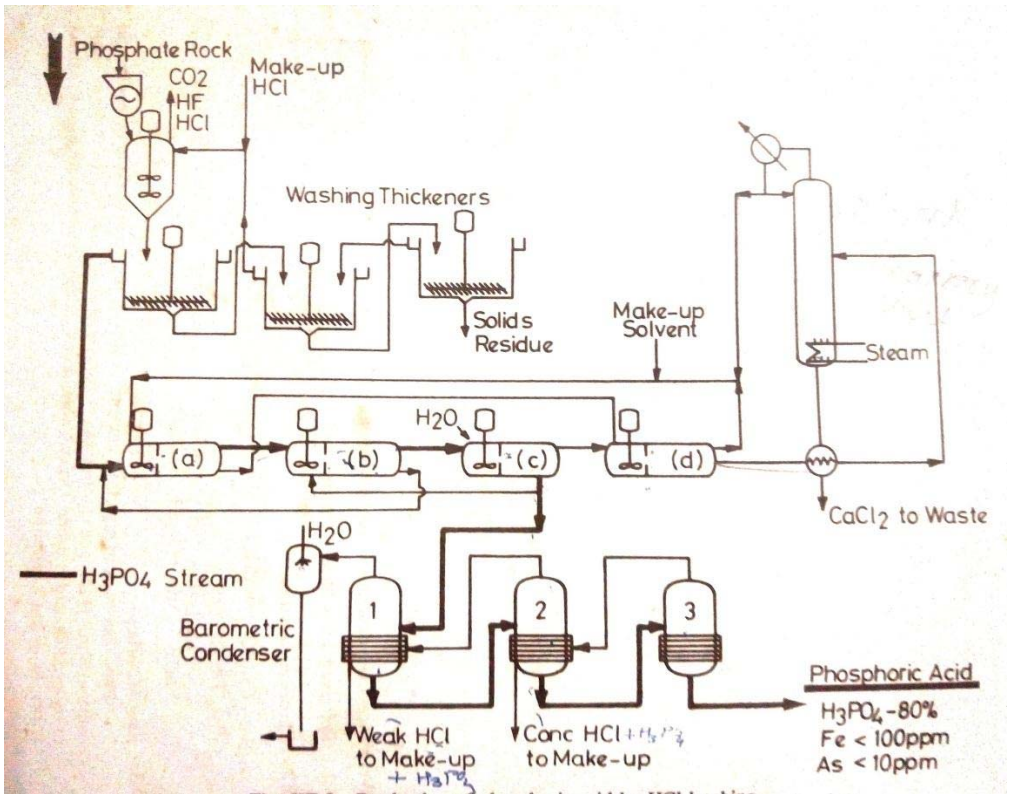
		flue gases at the time of heating. Hence cement contains very small quantities of alkalis in it. If alkalis content is more than 1% then it will cause several problems like alkali aggregate reaction, efflorescence, staining etc.	
	b)	**Hydrogen from water gas (Bosch Process)** In the Bosch process, large quantities of hydrogen are produced from cheap raw materials such as water and coke. When steam is passed over red hot coke (carbon) at a temperature of about 1200^0C, a mixture of carbon dioxide and hydrogen is produced. Excess steam is then mixed with the water gas [carbon dioxide and hydrogen] and passed over a catalyst which could either be iron oxide or chromium oxide, at a temperature of about 450^0C. The resultant effect is that the carbon dioxide in the water gas is converted to carbon monoxide with a further yield of hydrogen. The first reaction, which is the production of water gas is endothermic, while the second reaction which is the reduction of steam to hydrogen by carbondi oxide, is exothermic. The carbon monooxide is then removed from the mixture by dissolving it in water under pressure of 30 atmospheres or in other solvents such as caustic soda solution. Any unreacted carbon dioxide is absorbed in ammoniacal solution of copper ethanoate.	4
	c)	**PFD of Sulfuric acid production** 	4

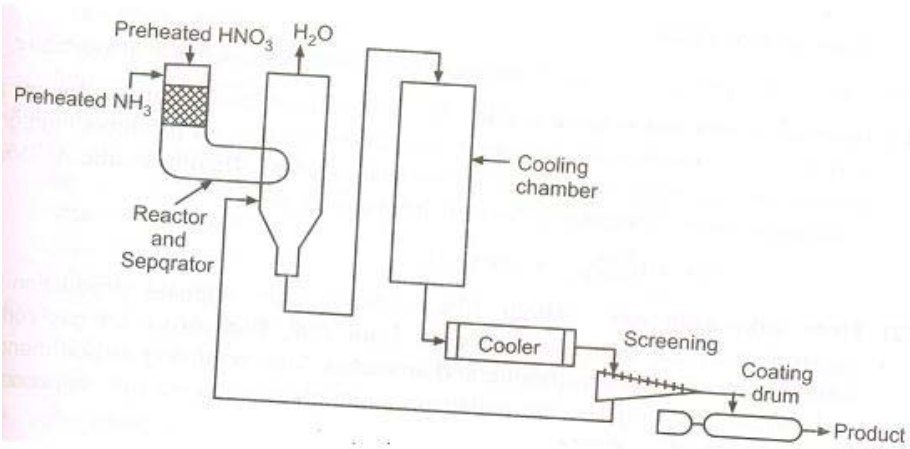
	d)	**Ammonia** Raw Material • Synthesis gas as a source of hydrogen • Air as source of nitrogen Reaction : $N_2 + 3H_2 = 2NH_3$	2 2
4		**Attempt any three of the following**	**12**
	a)	**Triple superphosphate** This material is much more concentrated fertilizer then ordinary superphosphate it contains from 45 to 46% of available P2O5 of nearly three times the amount in the regular superphosphate. Chemical reaction: $CaF_2.3Ca_3(PO_4)_2 + 14H_3PO_4 \longrightarrow 10Ca(H_2PO_4)_2 + 2HF$ It is made by action of phosphoric acid on phosphate rock. The pulverized phosphate rock is mixed with phosphoric acid into a two stage reactor. The resultant slurry is sprayed into the granulator The product from the granulator is dried, screened, the oversize crushed and cooled again. Final product is conveyed to bulk storage where product is cured 4 to 6 weeks. During curing further reaction of acid and rock occurs which increases the availability of P_2O_5 for plants as food. Exhaust gases from granulator and cooler are scrubbed with water to remove silicofluorides. 	2 2

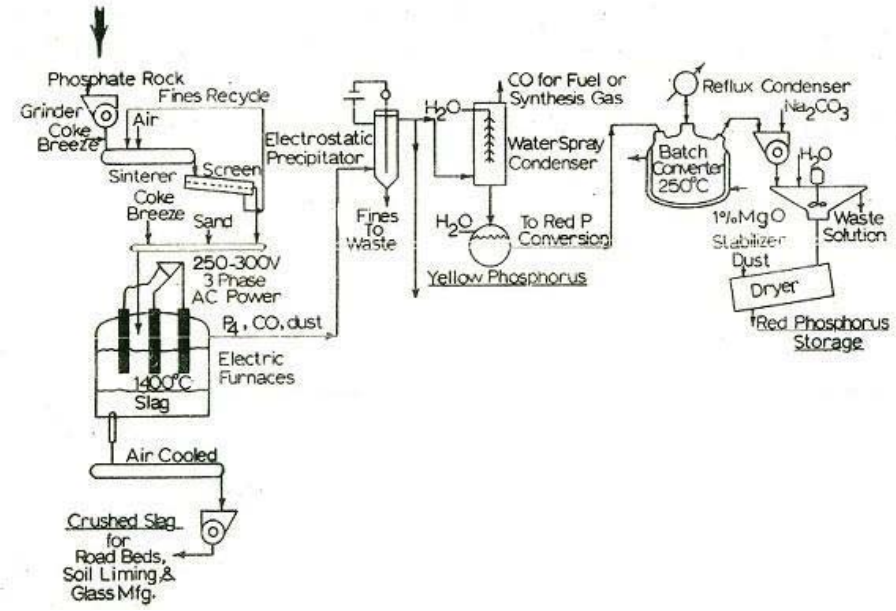
	b)	**Manufacturing Process of chlorine** Purified saturated brine is heated and electrolyzed in a diaphragm cell. The cell operating at 45-55% decomposition efficiency, discharges 10-12% solution of caustic soda with about equal concentration of NaCl. Multiple effect evaporator concentrates the cell liquor to 50% NaOH solution The opted salt is separated, centrifuged, washed, then slurried with treated brine. Salt saturator overflow is 50% caustic soda product. This further brine is again treated the mercury cell and the yield from this section is 70% of caustic soda. Chlorine is collected, dried, compressed and cooled upto-30^{o}C and collected as liquid chlorine. Or **Electrolytic Process:** In this process carbon dioxide is passed in the solution of sodium hydroxide obtained by the electrolysis of aqueous solution of sodium chloride. $2NaOH + CO_2 \longrightarrow Na_2CO_2 + H_2O$ The electrolysis of sodium chloride is carried in an iron box lined with bricks. A carbon rod is used as the anode and copper wire gauze covered on the inside with asbestos serves as the cathode. A concentrated solution of sodium chloride is admitted into the cell at the bottom and the electrical current is passed through it. As the solution rises it undergoes electrolysis and finely leaves the cell from the top as spent liquor. $2NaCl \longrightarrow 2Na^{+} + 2\ Cl^{-}$ At cathode, $2H_2O + 2e^{-} \rightarrow 2OH^{-} + H_2$ At anode, $2\ Cl^{-} \rightarrow Cl_2 + 2\ e^{-}$ Thus chlorine is liberated at the anode and at the cathode sodium hydroxide and hydrogen are formed. Chlorine and hydrogen escapes from the respective outlets in the anode and cathode compartments. A mixture of steam and carbon dioxide is then blown into the sodium hydroxide solution in the cathode compartment when sodium carbonate is formed as mentioned earlier. The solution is periodically removed and concentrated to obtain pure crystalline sodium	4

		carbonate.	
	c)	**Good refractoriness** Refractoriness is a property at which a refractory will deform under its own load. The refractoriness is indicated by PCE (Pyrometric cone equivalent). It should be higher than the application temperatures. Refractoriness decreases when refractory is under load. Therefore more important is refractoriness under load (RUL) rather than refractoriness. **Refractoriness under load (RUL) (or) strength** The temperature at which the refractory deforms by 10% is called refractoriness under load (RUL). Refractories used in industries and in metallurgical operations, should bear varying loads. Hence refractories should have high mechanical strength under operating temperatures. Generally softening temperature decreases with increase of load. The load bearing capacity of a refractory can be measured by RUL test. ***Note: Marks should be given for properties of refractories***	4
	d)	**Manufacturing of CO_2** Combustion gases are mainly consists of carbon dioxide. To get pure carbon dioxide combustion gases must be cleaned and CO2 should be separated. These two important steps are carried out by absorption. Detailed process is given below. Flue gases result from burning carbonaceous material are cooled, purified and washed by passing through two water scrubbers contain Na_2CO_3. ($Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$) The reaction to left is formed by heating $NaHCO_3$.CO_2 is absorbed in absorber by counter current selective absorption. in aq. solution of ethanolamine CO_2 and steam passed through reactivator and then through CO_2 cooler to condensed steam which returns to the tower as reflux.CO_2 passes through permagnet scrubber where traces of H_2S amines are removed it is dried by passing it through dehydration drums. Finally CO_2 is condensed cooled in precooler and sent to liquid CO_2 receiver for liquefaction.	4
	e)	**Industrial Applications of mixed fertilizers** No industrial application. It is used as fertilizer.	4
5		**Attempt any two of the following**	**12**

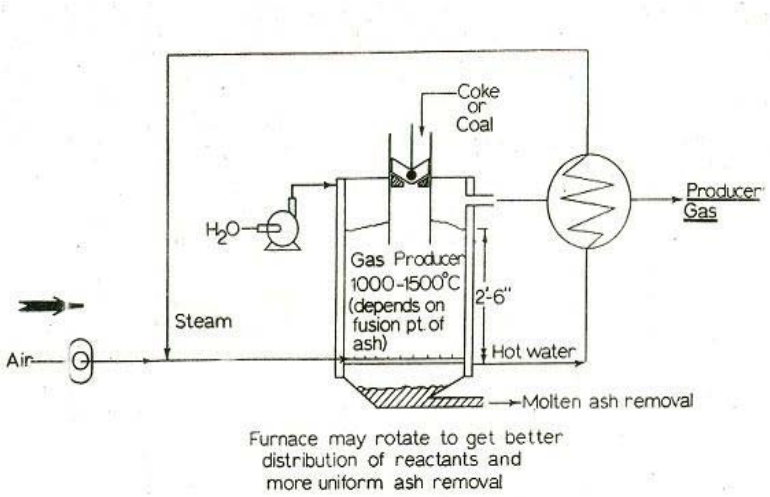
	a)	**Phosphoric acid by wet process** **1. H_2SO_4 leaching** Reaction: $Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O = 2H_3PO_4 + 3(CaSO_4.2H_2O)$  Process: Phosphate rock is ground and fed to chute where a recycle stream of weak phosphoric acid washes into reaction tank. Strong sulfuric acid is fed to the reactor. Around 98% conversion takes in 4-6 hours. Heat of reaction is controlled by using cooling air. Gypsum –Acid slurry is fed to travelling pan filter where 40% acid is removed and cake is washed with water. Filtrate is return to the reactor. The gypsum obtained is dried and send for paint or cement manufacturing. Dilute acid obtained can be concentrated in single effect evaporator. **OR** **2. HCL leaching** Phosphate rock is ground and HCl is added in it. Fumes of CO_2, HF and HCl are	Reaction and raw material 1 mark + process 2 marks + PFD 3 marks

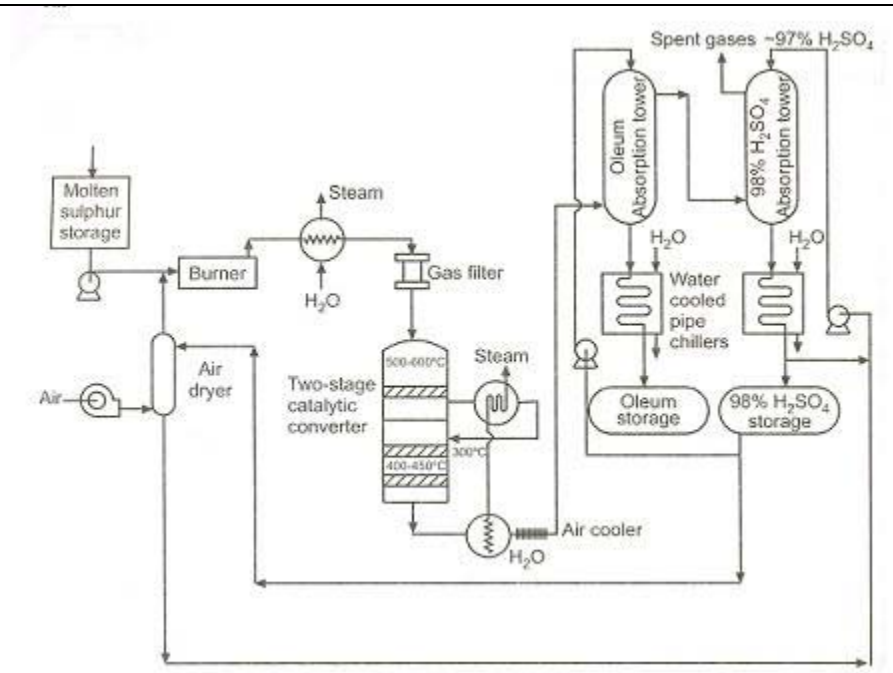
		scrubbed for acid recovery. The mixture is fed to series of decanter and settlers and then to counter current solvent extraction operations. The solids underflow goes to 2-3 washing thickeners. Extraction of phosphoric acid and some free HCl is done in an battery of mixer –settlers with $CaCl_2$ retain in aqueous phase. The extract is passed through several more mixer settlers. Phosphoric acid is recovered in triple effect evaporator and $CaCl_2$ is separated from final settler.  	
	b)	**Ammonium Nitrate** **Process description –** In the Stengel process, vapours of ammonia & nitric acid are mixed in a stainless steel reactor. The reaction is exothermic & hence heat is given out. The mixture of steam & molten ammonium nitrate is fed to cyclone type separator. The molten mass is solidified on the water cooled stainless steel belts .Then material is passed to a grinder where is the material is crushed dried and ground to flake size then, ammonium nitrate flakes are coated with clay.	2

		Reaction $HNO_3 + NH_3 \rightarrow NH_4NO_3$  	1 3
	c)	**Red phosphorus is used in production of match boxes.** **Red Phosphorous Production** Raw material: Phosphate rock, coke, sand Reaction: $2Ca_3(PO_4)_2 + 10C + 6SiO_2 = P_4$ (Yellow) + 6 $CaSiO_3$ + 10CO P_4 (Yellow) + heating = P_4 (Red) Phosphate rock is ground, mixed with portion of coke requirement, then sintered into nodules to obtain better electrical resistivity characteristics and to avoid entrainment of fines in the released phosphorous and carbon monoxide vapors. Screening is necessary to maintain size control with fines recycled to the sintering operation. Coke breeze and sand particles are mixed in controlled quantities based on phosphate rock analysis.	1 2

		The electrical 3 phase furnace is at 230-300V designed with power fed to 100-150cm diameter carbon electrode on each phase. The feed charge drops gradually into the fused section of the furnace at 1400°C where the reduction to elemental phosphorous takes place. The furnace is kept under slight vacuum by fans in the downstream end of the plant , so the furnace gases moves to electrostatic precipitator to remove dust and then water cooled condenser. Liquid yellow phosphorous is collected under water. CO obtained is used as fuel. Molten slag obtained from furnace can be used as raw material for furnace. Yellow phosphorus is converted into red phosphorous in covered retorts containing a reflux condenser to retain any evolved phosphorous vapors. The vessel is gradually heated and the contents melt and slowly change to red phosphorus. This mass is solidified when approximately 70% has been converted. Heat control is required as reaction is exothermic.  	3
6		**Attempt any two of the following**	**12**
	a)	**Industrial application of soda ash**	1 mark each for any six

		In the manufacturing of - • Glass manufacturing • Soap/detergents • Pulp and paper • Desulfurization • Textile processing • dyes and coloring agents • used to improve and treat the alkalinity of lakes that have been affected by rain • used to remove or de-clarify phosphates and sulfurs from a number of non-ferrous and ferrous ores • food additive used as an acidity regulator, anticaking agent, raising agent, and stabilizer	
	b)	**Producer gas**, It is a mixture of flammable gases (principally carbon monoxide and hydrogen) and nonflammable gases (mainly nitrogen and carbon dioxide) made by the partial combustion of carbonaceous substances, usually coal, in an atmosphere of air and steam. Steam and air mixture injected in the bottom of water cooled jacket steel furnace equipped with rotating grate to remove fusible ash as shown in figure. Solid fuel is added from hopper valve on the top. Producer gas is cooled by passing through waste heat boiler. There are various zones in gas producer. Formation of producer gas from air and carbon: $C + O_2 \rightarrow CO_2$, +97,600 calories $CO_2 + C \rightarrow 2CO$, -38,800 calories $2C + O_2 \rightarrow 2CO$, +58,800 calories Reactions between steam and carbon: $H_2O + C \rightarrow H_2 + CO$, -28,800 calories $2H_2O + C \rightarrow 2H_2 + CO_2$, -18,800 calories Reaction between steam and carbon monoxide:	3

		$H_2O + CO \rightarrow CO_2 + H_2$, +10,000 calories $CO_2 + H_2 \rightarrow CO + H_2O$, -10,000 calories  	3
	c)	**Sulfuric acid production** $S + O_2 = SO_2$ $SO_2 + ½ O_2 = SO_3$ $SO_3 + H_2O = H_2SO_4$ Description: Molten sulfur is oxidized with air in burner. Heat produced is recovered in waste heat boiler. Gas stream containing 7-10% SO_2 and 11-14 % O_2 preheated by convertor gas and send to first stage reactor . The reacted temp is 500-600° C contained 30% catalyst and convert about 80% of SO_2. The converter product exchange heat at 300°C and sent to second stage where yield is increased to 97% at 400-450°C .The product gases are cooled to 150°C by water and air heat exchanger and absorbed in oleum fed at rate to allowed not over 1% rise in acid strength. Final scrubbing is done with lower strength. **DCDA is double conversion double absorption. In sulfuric acid process sulfur is converted two times i.e. SO_2 and SO_3. SO_3 is absorbed in two scrubbers in series.**	1 2

		 Spent gases ~97% H_2SO_4 Oleum Absorption tower 98% H_2SO_4 Absorption tower Molten sulphur storage Steam Burner H_2O Gas filter H_2O H_2O Water cooled pipe chillers Air Air dryer Two-stage catalytic converter 500-600°C Steam 300°C 400-450°C Oleum storage 98% H_2SO_4 storage Air cooler H_2O	3