

Operating Experience of Black Liquor Desilication at APPM-Unit: Coastal

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ABSTRACT

The black liquor de-silication plant is established at The Andhra Pradesh Paper Mills Ltd., Rajahmundry Unit: Coastal Papers Ltd., Kadiam in East Godavari District of Andhra Pradesh. The Demo and Semi Commercial plant for de-silicating the black liquor generated from 30 tons of Rice Straw pulp per day was commissioned in March, 2007. This article deals with the commissioning experiences and the trouble shooting of the plant after commissioning.

Prior to the installation of the plant in depth pilot plant trials were conducted by CPPRI for finding out critical input parameters using their Pilot plant.

The de-silication is achieved by carbonation method of reducing the pH of black liquor to the precipitation level and separating them in conventional clarifiers by sedimentation process. The settled silica mud is pumped into a pressure filter for getting higher dryness before disposing. The de-silicated black liquor is being concentrated to 30- 35% BLS and sent to APPM by tankers for alkali recovery along with their black liquor.

At the moment, 70% de-silication is being achieved and still some more fine tuning and trouble shooting activities are to be carried out.

INTRODUCTION

Increasing per capita consumption of paper and paper boards and the ever reducing availability of wood based raw material has led to the increasing usage of secondary fiber and agricultural raw material in the paper industry in India.

The Andhra Pradesh Paper Mills (APPM), Unit: Coastal Papers at Kadiam in Andhra Pradesh is planning to establish a new Fiber Line Plant based on rice straw as raw material. Abundant quantity of rice straw is available to make 100 tons of pulp every day with in a 30 km radius from the mill. At present, the plant is equipped to make 30 tons per day of unbleached pulp from rice straw.

It is a known fact that it is extremely difficult to process the black liquor from Rice Straw as it contains a very high level of Silica. The high concentration of Silica poses problem at all stages of processing of black liquor. In the Evaporator, problems arise due to the formation of hard scales on the heat transfer surfaces due to which the plant capacity and availability tend to be badly affected. In addition, the increase in viscosity of the black liquor even at medium

concentrations results in severe problems associated with pumping and handling. In the Chemical Recovery Boiler, the high concentration of silica interferes with the reactions in the furnace. Further, the flow ability of smelt from the hearth through the spouts of the boiler is reduced, thereby plugged spouts are experienced very often affecting the availability of the boiler. The Physio-Chemical analysis of Rice Straw black liquor before and after desilication is presented in **Annexure - I**

Hence it is necessary to remove as much of the silica as possible from the rice straw black liquor before processing it for Chemical Recovery. This process is called "De-silication of Black Liquor". Due to the attractive cost of production of Rice Straw pulp and due to the abundant availability of the raw material near to the mill, APPM Unit: Coastal Papers decided to explore new technologies. Consequently, they approached Enmas Andritz (P) Limited, Chennai (EAPL) to install a

commercially viable demonstration (demo) plant. EAPL holds the license to commercialize the patented technology of Black Liquor De-silication held by M/S Central Pulp and Paper Research Institute (CPPRI) located at Saharanpur (UP) is the leading Central Government institution carrying out premium research and development activities for the Indian Pulp and Paper Industry. After extensive technical discussions between all the parties, APPM awarded EAPL the contract for engineering, supply, erection and commissioning of a plant to desilicate Weak Black Liquor (WBL) emanating from the existing wash plant. In order to contain the capital cost of the demo plant, it was decided that the tanks, pipelines and some pumps would be mobilized from APPM's surplus old causticizing and evaporator plants located in their major production facility 15km away.

Prior to the installation of the plant, in depth trials using the digester black liquor were conducted by CPPRI scientists. These trials were conducted

Table 1 Input conditions for desilication process

1)	RAA in WBL	4 – 5 as NaOH
2)	Silica present	6 – 13 gpl
3)	pH at max. removal of Silica	9.8
4)	pH of WBL before Silica removal	10.8 – 11.1

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***The A. P. Paper Mills Ltd., Rajahmundry (A.P)

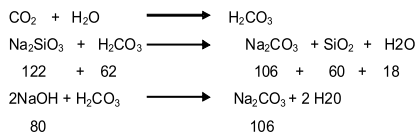
on CPPRI's pilot plant and the critical operational parameters were established. In addition, the requirements of input conditions necessary for the efficient operation of the de-silication process were identified as given in Table 1.

Accordingly, the plant was installed and commissioned in the month of March 2007.

CHEMISTRY OF DESILICATION

Silica is present in the rice straw raw material inherently as well as extraneously. During alkaline cooking, the silica dissolves into NaOH forming Na_2SiO_3 . The concentration of silica in WBL is as high as 10-13% on BLS basis. In the carbonation stage, CO_2 is dissolved in the water and forms carbonic acid.

The Sodium Silicate present in the



WBL is precipitated as SiO_2 and can be separated on sedimentation/filtration. The Sodium Silicate is converted to Na_2CO_3 by the reaction of CO_2 .

The range of pH at which Silica precipitates varies from black liquor and is dependent upon the nature of raw material used. The carbonic acid also reacts with residual active alkali NaOH to form Na_2CO_3 .

During the process, the % solids of the WBL get reduced due to removal of SiO_2 . However, conversion of NaOH to Na_2CO_3 increases the solids content. The dissolved CO_2 gas in black liquor also increases the solid content. The material balance of the solids is hereby given for 1m³ of WBL processed in desilication in **Annexure IIA & IIB**

The drop of pH lies in very critical range and if not controlled, there is chance of precipitating lignin also. Care should be taken to avoid precipitation of lignin during operation. It reduces the heating value of the BLS as well as

creating problems during filtration of silica mud. The consumption of carbon-di-oxide is proportional to the Na_2SiO_3 and residual alkali present in WBL.

SCHEME DESCRIPTION

The flow chart of the process de-silication as installed in APPM Unit: Coastal Papers, Kadiam is presented in **Annexure III**. The WBL from brown stock washers is taken to storage tank. The WBL is pumped to reaction tank (SRT-1) with the help of a Feed Pump. The flow is measured with the help of magnetic flow meter and is being controlled at a uniform rate with the help of control valve. The temperature of WBL is also measured on line with the help of thermo couple.

The SRT-1 is a big tank and adequate margin is kept for accommodating the foam generated during process. The tank is also provided with a high capacity circulation Pump. It is circulating WBL from tank to tank. Flue gas is injected into the WBL in the delivery pipe line of the circulation pump with the help of a suitable nozzle. The pH is brought down to the required level in stages in SRTs. The WBL is tapped off from the middle level of the tank in to the SRT-2 by gravity flow.

SRT-2 and SRT-3 are similar to SRT-1 and gas is injected in the delivery of the respective circulation pumps. Finally, the pH of SRT-3 outlet is maintained at desired level.

The CO_2 present in flue gas of coal fired boiler (around 10-12% by vol.) is used for carbonation reaction. The flue gas from the Coal Fired Boiler is pumped to the nozzle with the help of blower. Before the blower, the flue gas is scrubbed through the water to trap off the fine carbon particle and condense the water vapor present in the flue gas. The carbonated WBL is taken to Hot Retention Tank to complete the reaction.

The WBL from the HRT is pumped to clarifier feed well, for settling the precipitated silica (SiO_2). The under flow is taken with the help of a screw pump and fed to a pressure filter for separating the silica at increased dryness. The filtrate is taken back to polishing tank or to the clarifier for reducing the losses in the system. The foam generated in SRT-1, 2, 3 and hot retention tank are collected in to a foam

TABLE-2 FIBERS AND FINES CONTENT IN WBL:

DATE dd/mm/yy	TIME 00:00hrs	FIBER CONTENT ppm
20/10/07	18:00	37
21/10/07	19:00	128
23/10/07	08:00	70
25/10/07	08:00	70
26/10/07	12:10	336
28/10/07	11:00	54
29/10/07	08:00	160

TABLE-3 Analyzed by filtering over 100 mesh and collecting the fiber in a filter cloth
FILTER CAKE ANALYSIS:

DATE	% SOLIDS		FILTER	CAKE	ANALYSIS		SILICA As $\text{SiO}_2\%$
	BEFORE	AFTER	MOISTURE	ORGANICS	INORGANICS		
			%	%	%		
3/06/07	5	4.9					
7/06/07	5.88	4.88					
9/6/07	5.82	5.33	63.7	18.96	81.04		73.6
10/6/07	5.23	4.76	59.2	19.02	80.98		73
11/6/07	5.27	4.42	64.2	20.9	79.1		70.1
17/6/07	5.52	5.2					

tank where it is treated for reducing foam menace in the system.

Parameters	Original B.L	Desilicated B.L
pH at 30° C	12.0	10.3
Total Solids, %w/w	14.1	9.6
RAA,gpl as NaOH	11.0	0.8
Silica, gpl	13.3	0.68
Sulfur, %w/w	0.06	0.1
R2O3, % w/w	0.09	0.05
Organics, % w/w	67.65	71.9
Inorganics, % w/w	32.2	28.1
Calorific value, cal/g	2578	2940
Carbon, % w/w	34.4	36.6
Hydrogen, %w/w	2.5	2.9
Nitrogen, % w/w	0.7	1.0
Sodium, % w/w	8.5	11.5
Calcium,% w/w	0.04	0.06
Sulfate, %w/w as SO4	015.	0.15
Viscosity at 90°C(50% Total solids)	200 mPa.s	61 mPa.s

PLANT OPERATION

The demo plant after completing erection and commissioning trials started running on continuous basis since APR '07. The percentage of desilication achieved during OCT '07 is varying in the range of 67% - 86%. If the initial concentration SiO₂ in WBL is more, the % desilication is also high. The residual SiO₂ presents in the desilicated black liquor always lies in the range of 2.4 to 2.6% (based on BLS). The operating parameters are presented in **Annexure IV**

The silica concentration in de-silicated black liquor stays at equilibrium range of 2.4-2.6%. Hence for maximum removal of silica one should aim at higher inlet concentration.

The de-silicated black liquor is evaporated to 30 -35% concentration in 6 effect evaporator plant. This is also an old plant mobilized from APPM unit. The semi-concentrated black liquor is sent to APPM by tankers and mixed with their black liquor for further chemical recovery process.

As the plant is in operation first time in India some problems were also encountered during commissioning and in operation. They are as follows:

- 1) The feed rate 10 m3/hr of WBL could be achieved against 20 m3/hr of design.
- 2) Temp. of 52-54 ° C of WBL could be received from Pulp Mill against 70 ° C. Best desilication could be achieved at 70° C.
- 3) Pressure filter is able to discharge 2 batches only per day against 5-6 batches, as envisaged.
- 4) Carry over of Silica particles in the clarifier over flow due to foam is slightly more with more fiber content and lower temperature of the WBL
- 5) Difficulty in maintaining the pH of the WBL at various reaction tanks.
- 6) Clogging of the flue gas nozzles very frequently. The fine nozzle holes are getting clogged with precipitated Silica and fiber content present in the WBL. It is

ANNEXURE III/A

MATERIAL BALANCE OF SILICA AND RAA (De-Silication Plant)

Dt.11/12/07

FLOW m3	1	RAA as NaOH (gpl)	0.4
SILICA as SiO ₂ gpl	10	Silica as SiO ₂ gpl	2
RAA as NaOH (gpl)	4		
Reduction is Silica %	80		
BLS in WBL %	6		
Sp. Gravity of WBL	1.03		

BASIS: 1m3 OF WBL @ 6% CON.		WBL density		1030 kg/m3		
INPUTS:						
Black liquor:						
		Na	Si	moles O2	H2	C
Solids	61.8					
Water	968.2					
Sodium Silicate	20.33	0.333	0.167	0.250	-	-
Residual Active Alkali	4	0.100	-	0.050	0.05	-
Carbon Dioxide	7.85	-	-	0.178	-	0.178
		0.433333	0.166667	0.478333	0.050	0.17833
OUTPUTS:						
Black liquor after carbonation:						
Silica as Na ₂ SiO ₃ gpl	4.07	0.0667	0.03333	0.050000	-	-
Silica converted to Na ₂ CO ₃	14.13	0.266667	-	0.2000	-	0.133333
Residual alkali as NaOH	0.40	0.01	-	0.005	0.005	-
Alkali converted to Na ₂ CO ₃	4.77	0.09	-	0.0675	-	0.045
Silica removed as SiO ₂	8.00	-	0.133333	0.133333	-	-
Water as such	0.81	-	-	0.0225	0.045	-
		0.43333	0.16667	0.47833	0.050	0.1783

ANNEXURE - II/B

MATERIAL BALANCE OF SILICA & RAA				$\text{Na}_2\text{SiO}_3 + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{SiO}_2$			
Basis: 1m ³ of WBL				122	44	106	60
				$2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$			
FLOW	m ³	1		7.85	80	44	106
SILICA as SiO ₂	gpl	10		CO ₂			
RAA as NaOH (gpl)		4					
Reduction in Silica %		80		WBL	1030		
BLS in WBL %		6					
Sp. Gravity of WBL		1.03					
					1029.85		
							RAA as NaOH (gpl) 0.4
							Silica as SiO ₂ gpl 2
							SiO ₂ ↓ 8.00 kg
INPUTS:				OUTPUTS:			
	As such		kg		As such		kg
Silica as SiO ₂	10	20.333	(solid)	Silica as Na ₂ SiO ₃ gpl	4.07	(S)	
Residual alkali as NaOH	4	4	(solid)	Silica converted to Na ₂ CO ₃	14.13	(S)	
CO ₂ for conversion & de-alkalization	7.85			Residual alkali	0.4	(S)	
TOTAL		32.18		Alkali converted to Na ₂ CO ₃	4.77	(S)	
				Silica removed as SiO ₂ (ppt Solids)	8.00	(S)	
				Water as such	0.81		
				TOTAL	32.18		
Solids in original solution		24.333		Solids after carbonation		23.37	
BEFORE				AFTER			
Total Solids in WBL	kg	61.8		Total solids in WBL	kg	60.84	
Solids related to Silica & RAA	kg	24.33		Solids after conversion	kg	23.37	
Wt. of WBL	kg	1030		Wt of WBL after carbonation	kg	1029.85	
% solids	%	6		% Solids after carbonation	%	5.91	

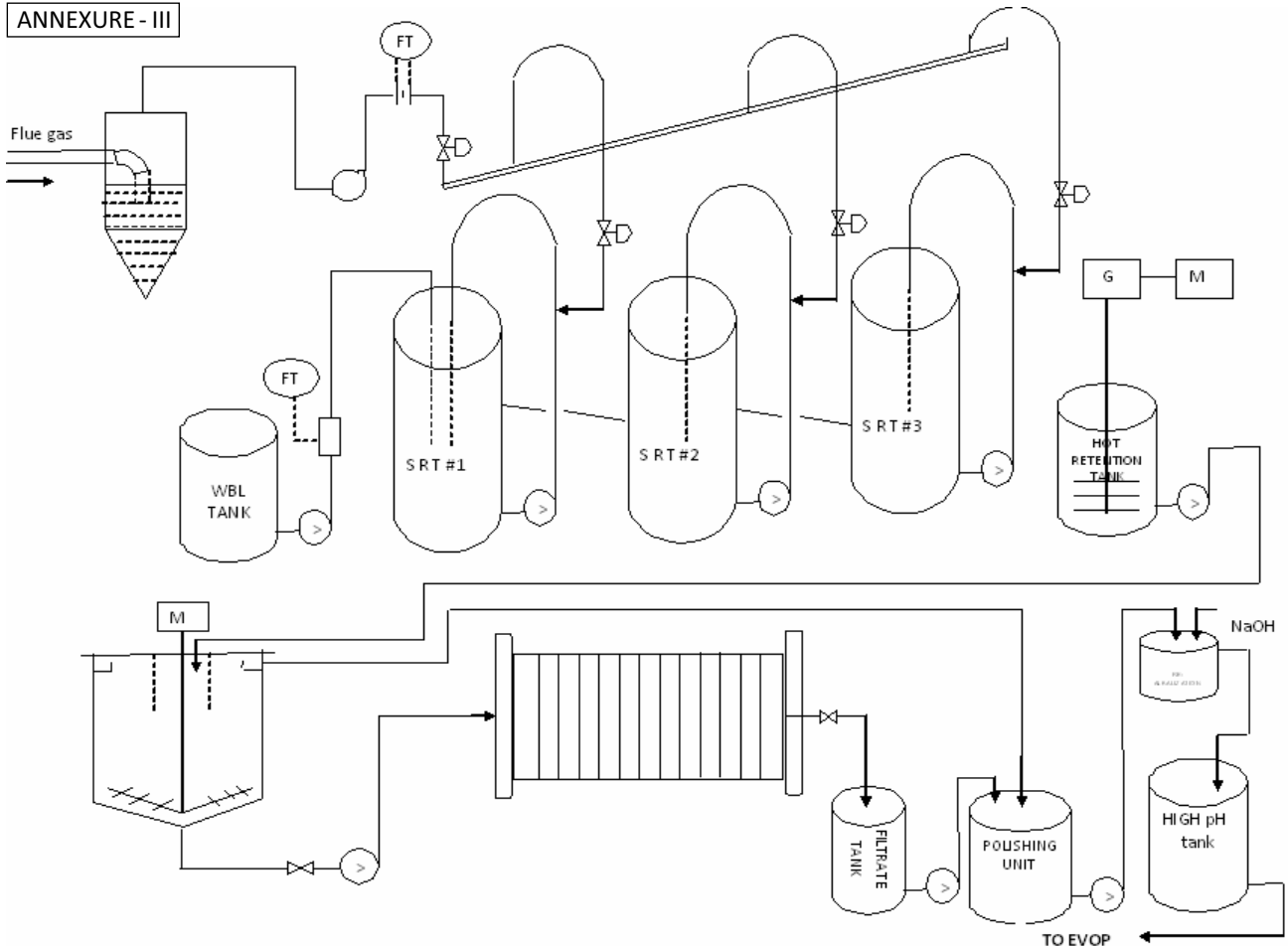
found difficult to remove nozzle for cleaning and maintenance as they are located at a very high elevation.

The problem of filter operation was attended by providing a compressed air line to the pressure filter. This helped in getting the cake dryness to 40-45% and thereby the cloth is cleaner and the time for washing the cloth after each batch got reduced. We could reach 4 batches a day from the previous of 2 batches.

The flow meter installed in the flue gas line is not functioning properly due to accumulation of water in the impulse line. It is attended by shifting the transmitter above the orifice (sensing element). It is to be connected to the flow controller to maintain constant flow of flue gas.

The bigger size nozzle was made into 4 Nos of small size nozzles for easy handling and easy maintenance purpose. The minimum pressure of the flue gas is being maintained at nozzle inlet.

ANNEXURE - III



ANNEXURE - IV

THE ANDHRA PRADESH PAPER MILLS LTD.,
Unit: COASTAL PAPERS Ltd, KADIAM (A.P)

B.L. DE-SILICATION PLANT OPERATING PARAMETERS

DATE	WBL CONSPN m3/DAY	RUNG hrs	WBL FLOW m3/hr	pH			FILTER BATCHES #	NaOH CONSPN kgs/Day	SILICA ON TS BASIS %			SILICA REMOVED %
				SRT - 1	SRT - 2	SRT - 3			WBL FEED	GLC O/F	HIGH pH	
10/01/07	80	6		10.4 - 10.63	10.2 - 10.4	10.0 - 10.04	0	472				
10/02/07									13.7	3.68	3.83	71.9
10/09/07	PLANT STOPPED FOR MODIFICATION OF PAPER M/C NO PULPING											
1 10/10/07	215	20	10.8	10.72 - 10.6	10.7 - 10.4	10.0 - 10.01	3	930	12.5	2.85	2.77	77.8
2 10/11/07	170	14	12.1	10.8 - 10.6	10.55 - 10.36	10.35 - 10.2	2	506				
3 10/12/07	162	19	8.5	10.9 - 10.6	10.5 - 10.6	10.2 - 10.31	2	750	12.6	4.19	3.71	70.6
13/10/07												
15/10/07	PLANT REMAINED SHUT NO PULPING											
4 16/10/07	88	7	12.57	10.78 - 10.7	10.5 - 10.55	10.2 - 10.36	0	124				
5 17/10/07	204	19	10.74	10.74 - 10.6	10.5 - 10.32	10.25 - 10.05	0	694	8.1	2.97	2.42	70.1
6 18/10/07	103	10	10.30	10.8 - 10.7	10.5 - 10.55	10.24 - 10.0	0	299				
7 19/10/07	57	6	9.50	10.72 - 10.6	10.52 - 10.43	10.15 - 10.22	3	197				
8 20/10/07	153	15	10.20	10.78 - 10.7	10.54 - 10.4	10.3 - 10.22	1	472				
9 21/10/07	206	20	10.30	10.74 - 10.6	10.35 - 10.56	10.0 - 10.29	1	671				
10 22/10/07	206	19	10.84	10.82 - 10.6	10.35 - 10.55	10.0 - 10.2	1	757	12.2	5.25	1.6	86.9
11 23/10/07	255	24	10.63	10.8 - 10.75	10.12 - 10.38	9.98 - 10	2	922	12.5	4.6	3.75	70.0
12 24/10/07	218	20	10.90	10.8 - 10.6	10.5 - 10.37	10.12 - 10	2	732	15.7	4.6	3.75	76.0
13 25/10/07	15	1.5	10.00						11.6	2.33	2.1	61.9
14 26/10/07	242	19	12.74	10.81 - 10.7	10.55 - 10.42	10.28 - 10.42	3	732	10	3.08	2.24	77.6
15 27/10/07	275	20.75	13.25	10.78 - 10.9	10.65 - 10.5	10.08 - 10.45	3	581	14.6	4.07	3.09	78.8
16 28/10/07	278	24	11.58	10.82 - 10.6	10.59 - 10.38	10.1 - 10.04	5	745	11.9	2.93	2.47	79.2
17 29/10/07	225	18	12.50	10.72 - 10.3	10.52 - 10.35	10.3 - 10.1	5	496	11	3.12	2.61	74.5
18 30/10/07	265	21	12.62	10.64 - 10.8	10.42 - 10.55	10.3 - 10.08	4	709	11.8	3.88	3.88	67.2
19 31/10/07	292	21	13.90	10.6 - 10.78	10.35 - 10.55	10.15 - 10.05	4	669	15.1	4.22	4.52	70.1
20 11/01/07		14					4		14.2	5.44	4.1	71.1

Removal of settled mud from the clarifier at higher rate, maintaining the WBL temperature at 70 °C and reducing the carryover of silica particles are under study and can be resolved in due course.

The operating parameters for about 14 days in the month of October '07 are presented at **Annexure - IV** From this data of % De-silication 'Y', pH of SRT 3 'S' and WBL feed rate 'P' a regression equation was worked out as given below: It is detailed in **Annexure - V**

$$Y = (-0.6139)*P + 0.0000032 * S + 82.28$$

From the above equation, the projected desilication at 20 m3/hr of WBL, desilication rate is coming out around 70% which is a fair figure. However, the aim of 85% is to be achieved and more studies and trouble shooting is to be carried out.

CONCLUSION

- Since APR '07 the plant is running on continuous basis and the desilicated black liquor at 30-35% concentration is being mixed with the APPM liquors for further chemical recovery process. Thus major problem of pollution is affectively taken care by APPM Unit: Coastal papers, Kadiam besides recovering chemicals from rice straw black liquor.

- At present the filter cake of SiO₂ having 70-73% silica content is being used for land filling in the mill premises only. The filter cake can be processed further to find use in rubber industry etc., in future for effective disposal.

- On line measurement of pH is to be established in the full scale plant for control of pH to get more efficient de-silication. The pH sensing probe is getting coated due to silica precipitation and becoming ineffective.

- The process proved to be a success and becomes a pioneering plant for other Rice Straw users.

ANALYSIS OF SAMPLES

The analysis of the sample for finding out silica content at various stages, silica cake analysis fiber content of WBL feed are mentioned below in tables 2 & 3.

ANNEXURE - V

S#	DE-SILICA-TION %	W.B.L flow m3/hr	SRT 3 pH	PY	P^2	PS	SY	S^2
	Y	P	S					
1	77.86	10.8	10.05	840.89	116.64	108.54	782.49	101.00
2	70.58	8.5	10.255	599.93	72.25	87.17	723.80	105.17
3	70.12	10.74	10.15	753.09	115.35	109.01	711.72	103.02
4	86.85	10.84	10.1	941.67	117.55	109.51	877.21	102.01
5	70.00	10.63	9.99	743.75	112.89	106.14	699.30	99.80
6	76.04	10.90	10.11	828.82	118.81	110.20	768.75	102.21
7	81.90	10.00	10.05	818.97	100.00	100.50	823.06	101.00
8	77.64	12.74	10.35	988.95	162.23	131.83	803.62	107.12
9	78.76	13.25	10.185	1043.85	175.64	134.98	802.20	103.73
10	79.19	11.58	10.07	917.30	134.17	116.64	797.46	101.40
11	74.45	12.50	10.2	930.68	156.25	127.50	759.44	104.04
12	67.20	12.62	10.19	848.03	159.24	128.59	684.79	103.84
13	70.07	13.90	10.1	974.25	193.34	140.44	707.67	102.01
14	71.13	14.00	9.8	995.77	196.00	137.20	697.04	96.04
TOTAL	1051.80	163.00	141.60	12225.94	1930.37	1648.25	10638.55	1432.40
AVEG.	75.13	11.64	10.11	873.28	137.88	117.73	759.90	102.31

$$Y = m_1P + m_2S + C$$

$$11.64m_1 + 10.11m_2 + C = 75.13 \quad \rightarrow \quad 1$$

$$Sig Y = m_1SigP + m_2 SigS + nC$$

$$163m_1 + 141.6m_2 + 14C = 1051.8 \quad \rightarrow \quad 2$$

$$Sig PY = m_1SigP^2 + m_2SigSP + CSigP$$

$$m_1, 1930.37 + m_2, 1648.25 + 163C = 12225.94 \quad \rightarrow \quad 3$$

$$m_1 = -0.61344$$

$$m_2 = 0.0756$$

$$C = 81.51$$

$$Y_{@20m3/hr \text{ and } pH9.8} = 20 * (-0.61344) + 9.8 * 0.0756 + 81.51 = 69.98$$