Trial Amine and Polymer Base Chemical to Enhance The Quality of Boiler Water System Daily Operation at RFCC Pertamina RU IV Cilacap

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Abstract. Chemical Boiler Internal Treatment (CBIT) is important to maintain steam quality. Utilities RFFC Cilacap have quality issue due phosphate hide out phenomena that cause corrosion at compressor Turbine. Improvement of CBIT through chemical base substitute is things done at the Boiler Utilities RFCC Pertamina RU IV Cilacap. The trial using polymer base & filming amine base. Evaluation parameters during the trial are the quality of steam, boiler water and surface condensate. Trial duration for amine base and polymer base are three months for each chemical. The trial is a plant test in boiler system Utilities RFCC RU IV Cilacap. Those chemicals achieved on spec parameter above 95%. Average ratio feed/blowdown for each chemical are 0,0861 for amine base and 0,1012 for polymer base compared with previous treatment 0,108.

Keywords: Chemical boiler internal treatment, Amine base, Polymer base

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1 Introduction

The boiler Water system at utilities RFCC RU IV Cilacap has steam pressure operation at 42 kg/cm2g. The quality of steam is maintenance by using phosphate treatment, trisodium phosphate, as chemical boiler internal treatment base. Application of phosphate refers to JIS standard, JIS B8223 Boiler feed water, boiler water and steam quality Table 3 Water Conditioning for feed water and boiler water tube boiler (circulation boiler) [1].

Table 1. Water Conditioning for feed water and boiler water tube boiler (circulation boiler)

Division	Normal Operating Pressure (MPA)	1 max	1 - 2	2 - 3	3 - 5	5 - 7
Type of Make-up water		Softener	Ion exchanged			
Boiler Water	Treatment	Alkali	Phosphate/Alkali			Alkali/Phosphate/Volatile matter

Aside from phosphate as chemical treatment, hydrazine and neutralizing amine are used to maintain quality of boiler water system. Hydrazine could remove oxygen content from boiler feed water. It prevents boiler tube get leaked from oxygen-Fe chemical reaction. Neutralizing amines maintain pH of condensate more than 7, alkaline condition. Neutralizing amine and hydrazine are injected at outline deaerator as pressurized vessel boiler water feed difference with phosphate that injected separated at steam drum each boiler.

During phosphate treatment period 2015 – 2019, several time utilities RFCC RU IV Cilacap has accident with phosphate hide out phenomena. Phosphate hideout phenomena is condition where value of phosphate became lower when load of boiler rise and became high when load of boiler down [2]. The fluctuated value phosphate during that condition make adjustment of phosphate injection became difficult and create over range condition.

The adjustment control of the phenomena potentially rising the solid content inside boiler and create possibility of foaming accident higher. Foaming condition have some damage to water quality at boiler water system. Impurities inside boiler will harder separate and lead to steam brought more silica and create trouble at steam turbine equipment process. [3]

Silica carries over damages the turbine blade and decreases turbine isentropic efficiency [4]. The Inefficiency of turbine because silica content could accelerate corrosion at surface turbine [5]. Besides creating corrosion, silica content often deposits In the LP turbine and can change frequency of blade and rise centrifugal load of blade [6].

The Turbine corrosion and white deposit had found at major overhaul turbine at RFCC RU IV Cilacap. To prevent the repetitive condition or another future event of turbine the base treatment of boiler water system is substituted to non-phosphate treatment.

2 Methodology

Trial substitution was held by using two different chemicals, polyamine base as volatile matter treatment and polymer base as advanced phosphate treatment base with use different period. Interval between amine base and polymer base trial, the Amine base still injected to system. This Condition to prevent boiler water system get trouble and reduce performance and steam quality. During that period amine base still get evaluated periodically.

Table 2. Chemical Trial Period for Each Chemical Base

No	Chemical Base	Period
1	Amine Base	17 August 2020 – 14 November 2020
2	Polymer Base	18 February 2021 – 21 May 2021

The boundaries of trial are to keep water quality of boiler water system is stable, from boiler feed water to surface condensate. To make sure the quality is on spec, several parameters are used as detail table below and do sample analyses every 8 hours.

Table 3. Analyst Parameter for Each Stream

Parameter	Unit	Boiler Feed Water	Boiler Water	Boiler Steam	Surface Condensate
pH		8,5 – 10	9,4 – 10,5	8,5 – 10	8,5 – 10
Conductivity	Micro siemens/cm	10	600	10	10
Silica	ppm	0,02	10	0,02	0,02
Fe		0,02	0,5	0,02	0,02

Four parameters that analysis of each stream representative of internal boiler system condition. pH condition gave information about potential corrosion. Conductivity represents ionic content inside water that affects turbine compressor. Silica content to monitor separation phase inside boiler, if the silica is breakthrough to steam system it will affect the process area. Fe is an indicator for corrosion inside water boiler system if the Fe content rise will lead to assumption that corrosion happened.

Table 4. Equipment List for Water Sample Analysis

No	Equipment	Quantity	Remark
1	Boiler	3	Utilities Boiler
2	COB	1	Waste Heat Boiler HPS
3	Catalyst Cooler	2	Waste Heat Boiler HPS
4	Steam Generator	2	Waste Heat Boiler MPS
5	Steam Turbine	3	Utilities Turbine

	Generator		
6	MAB	1	Turbine Process Area
7	WGC	1	Turbine Process Area
8	HPC	1	Turbine Process Area

Dose and injection location of each chemical its difference depend on vendor recommendation, polymer base used 0,5 – 2,5 ppm and use injection system like phosphate treatment, directly at steam drum boiler. Amine base uses 5,0 ppm and injected at outlet deaerator like neutralization amine.

3 Result & Discussion

Polyamine selected as chemical base treatment refers to JIS B8223 that optional for chemical treatment at circulating boiler is volatile treatment [1]. Volatile treatment required better quality of feed water than phosphate treatment such as lower iron (50 ppb vs 100 ppb) and lower dissolved oxygen (7 ppb vs 30 ppb). The higher requirement Utilities RFCC RU IV Cilacap still could accommodate because Deaerator Equipment product specification is 7 pbb dissolved oxygen. Then quantity of iron at requirement higher than feed water. This condition is result of polisher package equipment that installed at Utilities RFCC RU IV, polisher have duty to remove all ion from water. Based on the condition had explain polyamine the first choice to enhance quality of boiler water system.

Polyamine has a complex structure, it has Cationic surface active, multi-component mixture of secondary & tertiary polyamine, organic polymers and dispersants. Primary and secondary amine have function to became buffer pH like neutralizing amine at phosphate treatment base additional chemical. Because has the same effect as neutralizing amine, polyamine do not need pH buffer chemical during operation. Then copolymer and surface-active cationic polyamine mixture component have function to capture bivalent cation such as Ca2+, Fe2+ and Mg2+. and capture Iron oxide and iron hydroxide. Furthermore, polyamine could create filming amine to protect internal part of boiler. This condition happens because the free electron pair of the amine nitrogen interacts with the metal surface. The interaction creates a not wet-able condition between water and metal surface, which offer a cohesive protection [7]. Even though polyamine could create filming amine to protect internal boiler, polyamine could not protect internal boiler from scaling event. Therefore, polyamine need higher requirement of feed water quality especially from hardness.

Amine base potentially gives satisfactory result at boiler water system but to create optional treatment and better economic impact, polymer treatment is selected to compare with amine base treatment. The expectation of polymer base will give better stability than phosphate treatment based on less doses than phosphate base. Another reason because Polymer has function to make condition where sludge non-adherent to boiler surfaces, so sludge can be easily removed in via blowdown same function of phosphate base but without create phosphate hide out condition. With that function, polymer base treatment needs additional chemical to maintenance reliability of boiler and downstream equipment such as condensate still need injection of neutralizing amine to keep pH high and corrosion caused by carbonate do not happen at condensate line. Then Oxygen scavenger to

remove oxygen before entering boiler equipment. Oxygen content in water at high temperature bring corrosion rapidly increase [8].

3.1 Boiler Feed Water

The average ratio of feed water and blowdown water during amine base and polymer base period are lower than phosphate base period 0,0861 for amine base and 0,1012 for polymer base compared to 0,108 at phosphate base. The lower ratio indicate there is no solid content formation inside boiler and could reduce the blowdown flowrate. The lower blowdown rate made the cost operation cheaper because the water cost caused by un-utilized water such as blowdown boiler could minimize.

Table 5. Ratio of Boiler Feed Water and Blowdown

Average Operating Condition										
No	Boiler	Phosphate Base			Amine Base			Polymer Base		
		Flow BFW (Ton/Jam)	Flow Blowdown (Ton/Jam)	Ratio	Flow BFW (Ton/Jam)	Flow Blowdown (Ton/Jam)	Ratio	Flow BFW (Ton/Jam)	Flow Blowdown (Ton/Jam)	Ratio
1	Aux Boiler A	56,59	0,555	0,0098	59,1	0,509	0,0086	57,07	0,368	0,0064
2	Aux Boiler B	54,10	0,535	0,0099	59,1	0,547	0,0093	56,95	0,642	0,0112
3	Aux Boiler C	54,25	0,449	0,0083	59,4	0,544	0,0092	57,57	0,610	0,0106
4	COB	185,32	5,645	0,030	168,48	4,126	0,024	152,17	5,532	0,036
5	Catalyst Cooler A	54,70	1514,04	0,027	50,7	1372,14	0,027	72,39	1343,37	0,018
6	Catalyst Cooler B	62,46	1,468	0,023	62,1	1,968	0,032	71,25	1,351	0,019
		Total		0,108	Total		0,0861	Total		0,1012

Lower solid content formation inside boiler caused by some reason. Amine based is volatile matter and the chemical will be brought with steam and leave boiler safely. Then Polymer base, even though the chemical is not volatile matter, the polymer has character sludge non-adherent to boiler surfaces dose so easily remove by blowdown then chemical dose lower than 2,5 ppm vs phosphate base around 8 ppm. Lower dose reduce the solid content formation possibility.

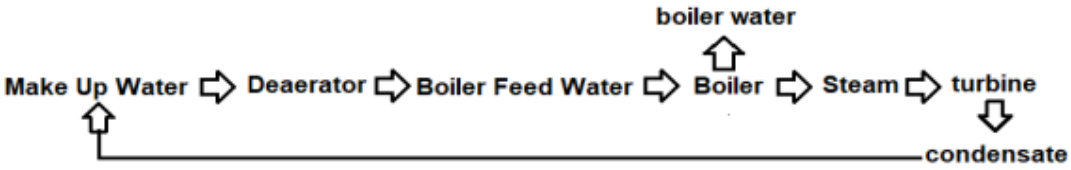

Fig. 1. Flow of Boiler Water System

The boiler water system at RFFC Cilacap use two source of make-up water, condensate and demineralized water. Demineralized water is water from raw water that had process through desalination step using thermal desalination and polishing using mix bed polisher. Condensate contributes to boiler feed water source more than 55% . Condensate from process is back to tank and mix with demineralized water before becoming boiler feed water. This flow process lead condensate product qualities gave big impact to boiler feed water.

Table 6. Resume Boiler Feed Water Quality

Parameter	Result						Target
	Average		Min		Max		
	Amine Base	Polymer Base	Amine Base	Polymer Base	Amine Base	Polymer Base	
pH	9,53	8,68	9,12	7,36	9,90	9,87	8,5 – 10,0
Conductivity (µs/cm)	6,49	2,05	4,40	0,34	7,30	8,11	≤ 10,0
Total Iron (ppm as Fe)	0,005	0,01	0,002	0,00	0,013	0,09	≤ 0,02

Demineralized water quality is controlled to give minimum deviation during amine base and polymer base treatment. The results show that both treatments could keep the average quality stable. Polymer base has several times the pH lower than requirement but still higher than 7.0. this condition happen because pH buffer, the polymer is injected at steam drum not deaerator vessel so if the pH condensate too low it will corrected after the feed water go to boiler equipment.

3.2 Chemical Dose

The average dose during trial period is lower than maximum estimated dose that had propose by the vendor. Amine base got 4,67 ppm vs 6 ppm, then polymer base got 0,57 ppm vs 2,5 ppm. The lower dose shows that the quality aspect of each stream is stable and did not need any adjustments.

Table 7. Average Actual Dose of Chemical

No	Chemical Base	Actual Dose	Estimated Dose

1	Amine Base	4,67 ppm	5 – 6 ppm
2	Polymer Base	0,57 ppm	0,5 – 2,5 ppm

3.3 Stream Quality

Amine base treatment gives result almost all requirement quality is achieved. Critical specifications such as silica steam quality and pH condensate got 100% on spec parameter throughout trial period. all equipment is operating normal without problem, it represented that filming amine created so problem such as boiler leak is mitigated. For polymer base treatment also give result almost all requirement quality is achieved even it is lower than amine base treatment but still higher than 95%.

Table 8. Resume Boiler Water & Steam Quality of Boiler Part 1

Parameter	Item	Range	Equipment							
			Boiler HP Steam				COB			
			Amine Base		Polymer Base		Amine Base		Polymer Base	
			Value	On Spec	Value	On Spec	Value	On Spec	Value	On Spec
pH	BW	9,4 – 10,5	10,16	100 %	9,73	99,74%	10,00	100 %	9,68	99,28%
	Steam	8,5 – 10	9,52	100 %	9,84	98,76%	9,54	100 %	8,7	99,63%
Conductivity	BW	Max 600	30,20	100 %	39,01	100,00 %	17,75	100 %	19,09	100,00 %
	Steam	Max 10	6,24	100 %	2,41	100,00 %	6,33	100 %	4,97	99,28%
Fe	BW	Max 0,5	0,11	100 %	0,13	99,63%	0,01	100 %	0,12	100,00 %
	Steam	Max 0,02	0,005	100 %	0,01	99,26%	0,006	100 %	0,01	99,28%
Silica	BW	Max 10	0,007	100 %	0,11	100,00 %	0,105	100 %	0,43	99,64%
	Steam	Max 0,02	0,007	100 %	0,01	98,87%	0,007	100 %	0,02	97,84%

This issue because Complexity of injection chemical could lead to inefficiency and ineffective chemical injection. To maintain pH of boiler water, use difference chemical with pH of condensate. Polymer chemical could maintain pH of boiler water but need neutralizing amine to maintain pH of condensate difference with amine base treatment that does not have function raising pH of boiler water. So, to maintain the quality, amine base keeps the pH condensate high enough to keep pH entire system before feed became steam and primary and secondary amine take in charge to maintain pH of water.

Table 9. Resume Boiler Water & Steam Quality of Boiler Part 2

	Equipment									
Parameter	Item	Range	Cat Cooler				Boiler MP Steam			
			Amine Base		Polymer Base		Amine Base		Polymer Base	
			Value	On Spec	Value	On Spec	Value	On Spec	Value	On Spec
pH	BW	9,4 – 10,5	10,06	100%	9,9	98,74%	10,09	100 %	9,66	99,74%
	Steam	8,5 – 10	9,535	100%	8,73	99,28%	9,52	100 %	8,76	99,46%
Conductivity	BW	Max 600	21,22	100%	41,815	100,00 %	22,94	100 %	16,26	100,00 %
	Steam	Max 10	6,21	100%	2,37	100,00 %	5,73	100 %	2,47	100,00 %
Fe	BW	Max 0,5	0,03	99,65 %	0,165	99,82%	0,01	100 %	0,14	99,46%
	Steam	Max 0,02	0,006	99,65 %	0,01	99,28%	0,007	100 %	0,01	99,64%
Silica	BW	Max 10	0,101	100%	0,175	100,00 %	0,096	100 %	0,13	100,00 %
	Steam	Max 0,02	0,0095	100%	0,01	98,74%	0,057	100 %	0,01	98,38%

There is no issue about separation steam product and boiler water product. The Quality is still on operating window each stream. The fluctuation of load each boiler gives no big impact either amine base or polymer base. Amine base gives better results than polymer base about operational condition. the small fluctuation of polymer base caused by the rate injection of the polymer. With the optimization of chemical dose for steam drum of each boiler made several times the quality got out of range.

Table 10. Resume Condensate Quality of Steam Turbine

Parameter	Range	Steam Turbine Generator				Steam Turbine Process Area			
		Amine Base		Polymer Base		Amine Base		Polymer Base	
		Value	On Spec	Value	On Spec	Value	On Spec	Value	On Spec
pH	8,5 – 10	9,48	100%	8,96	98,74%	9,56	100%	8,80	99,52%
Conductivity	Max 10	5,91	100%	4,42	100%	6,63	100%	2,22	100%
Fe	Max 0,02	0,007	100%	0,013	99,36%	0,005	100%	0,013	98,80%
Silica	Max 0,02	0,005	100%	0,01	98,43%	0,006	100%	0,01	98,44%

The negative side of polyamine is creating higher conductivity at condensate. The high conductivity is caused by amine decomposed at high temperature. [7] pH and Conductivity value of amine base treatment are higher than polymer base treatment. The higher conductivity of amine base is effect from amine decomposed when contact high temperatures [7]. Even though polymer base use neutralizing amine as additional chemical during treatment, the neutralizing amine only use to keep the pH of condensate difference with amine base treatment, all conditioning of operation use

polyamine as the only chemical. This condition made the conductivity of polymer base lower than amine base.

3.4 Optimalization Price of Treatment

Another aspect to consider is chemical price. The amine base price is 9% lower than phosphate treatment refers to actual dose of amine injection. The lower blowdown caused by stable condition of boiler water and steam quality could reduce wastewater. The results give a result that using amine base chemical have impact at environment and cost operation.

Table 11. Price Ratio for Each Chemical

No	Chemical Base	Ratio Price based on phosphate treatment
1	Amine Base	0,91
2	Polymer Base	0,43
3	Phosphate Base	1

Polymer base has better cost efficiency of chemical price, it reduces 57% price compared to phosphate base. The lower price is caused by the less injection chemical. However, polymer base need higher blowdown than amine base although still lower than phosphate treatment. This condition happens because to maintain quality of stream for fluctuate load. Another positive thing about using polymer base than phosphate base is phosphate hide out potential event could reduce to near zero.

The chemical price could be different for each condition of chemical procurements tender. Amine base or polymer base could be at the same price but to make more an affordable and competitive price another chemical or vendor.

4 Conclusion

The polymer base and Amine base have better impact to reduce wastewater and cost chemical than phosphate treatment. These treatments also have better stability that lowering carry over silica potential at boiler water system. To create better efficiency polymer base and amine base treatment could compete at chemical procurement from different vendors without worrying about the quality and safety aspect of boiler operation.

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