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APPROACH TO ACHIEVE COMPLIANCE WITH WASTEWATER DISCHARGE REGULATIONS IN BRAZIL FOR BY-PRODUCT COKE PLANTS[1]

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Abstract

Wastewaters from By-product Coke Oven Plants are among the most difficult-to-treat industrial wastewaters and present unique challenges to achieve the stringent discharge regulations now effective in Brazil. ENVIRON has designed numerous biological treatment systems to remove (in sequence of regulatory requirements) Phenolics, Thiocyanate, Ammonia-nitrogen, and finally Nitrate-nitrogen. Now physical-chemical treatment processes are required to achieve low levels of for Total Cyanide, Selenium, Fluoride, and COD. The presentation will include concepts and selected details from recent coke plant projects, including several from Brazil. Key items to be addressed include methods for biological treatment of coke oven wastewaters for organics and total nitrogen removal, and treatment methods for Total Cyanide, Selenium, and Fluoride compliance. Key performance data will be presented to demonstrate the approach and concepts presented.

Keywords: Coke plant wastewater biological treatment; Nitrification; Denitrification; Cyanide; Selenium; Fluoride removal.

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1 INTRODUCTION AND BACKGROUND

Process wastewaters from coke plants have a wide range of pollutants including toxic compounds, and can be difficult to treat. Very sophisticated and complex treatment plants are required for consistent and reliable compliance with the strict discharge limits now required. As shown in Table 1, raw coke plant wastewaters are characterized by relatively high concentrations of phenolics, ammonia-nitrogen, and thiocyanate. Significant levels of the toxic compounds free cyanide and free sulfide are also present. Other parameters of concern include oil and tar, heavy metals including selenium and mercury, several inorganics including fluoride, and poly aromatic hydrocarbons including benzene and benzo(a)pyrene (BaP).

Table 1. **T**ypical coke plant process water characteristics

Parameter	Concentration Range (mg/L)	
	Raw	**After Distillation**
Total Phenolics	400-800	400-800
COD	2,000-5,000	2,000-5,0000
Oil and Tar	100-300	--
Total CN	100-300	<5-10
H_2S	500-200	<5-10
Total NH_3-N	6,000-10,000	100-500
Thiocyanate	200-2,000	200-2,000
Selenium	--	0.5-2.0
Benzene	10-50	<10
Fluoride	50-100	50-100

2 COKE OVEN WASTEWATER TREATMENT TECHNOLOGY REVIEW

Most coke plants utilize an ammonia distillation system for removal of free cyanides, .free sulfides, free ammonia, and fixed ammonia, followed by activated sludge treatment for organics removal and residual ammonia nitrification. Before the still system, the wastewater is stored for equalization or flow balancing and pretreated for oil and tar recovery. In China, the concept of free-fixed distillation approach is not well understood, leading to elevated levels of cyanide in the still system effluent. This approach would require significant additional costs for cyanide removal before discharge.

After the still system, additional equalization is commonly provided. The activated sludge process is the most commonly encountered biological treatment system in the industry. Although other forms of biological treatment can be employed, since activated sludge is by far the most common, it is discussed in this paper.

Relatively high MLSS/MLVSS levels (MLSS concentrations of about 7,000 to 10,000 mg/L, and higher at a few plants) are commonly used in the industry. These levels are higher than commonly found in other industrial wastewater applications, and are used to provide maximum system stability to allow consistent nitrification, especially with known toxic and inhibitory feed constituents (i.e., free cyanide, free sulfides, and ammonia). Another characteristic of coke plant treatment systems is the relatively low overflow rates (as low as 40 gal/day-sq ft) for the secondary clarifiers. This allows the higher MLSS/MLVSS levels mentioned above, while maintaining a high level of conservatism in the clarifier design.

An activated sludge design loading rate or other process design parameter is not widely used or available that can reliably be used for system design of coke plant systems. Several sources indicate that 3 to 5 days of hydraulic residence time are required for stable treatment. Sludge age is another parameter sometimes used to indicate the relative size of these systems, but is not universally applicable to all coke plant wastewaters. Through experience, we have developed several other process design parameters that can be used in design and operation of these systems. They will be discussed herein.

The addition of dilution water is commonly used in the industry, at rates of 50 to 200 percent of the feed flow, although regulators in some countries, including Brazil, discourage (or strictly forbid) such additions. Some plants may not be aware of the miscellaneous dilution water sources in their process water system. These include steam condensate, pump and conservation vent seal waters, freeze protection water, and storm water.

As mentioned above, nitrification is now commonly practiced in coke industry activated sludge systems. Until recently denitrification has not been widely used. The first full scale nitrification-denitrification system was installed 10 years ago and due to its success, the use of anoxic zones to reduce nitrate concentrations is now used in new plants. It is cost effective to include denitrification to reduce aeration energy costs and chemical alkalinity costs. Further, without it, high levels of nitrates would be present at the inlet to the secondary clarifiers. This typically leads denitrification in the secondary clarifier and floating sludge and foam in the effluent. Also, in some countries effluent levels of nitrates are regulated or reported to the public as a toxic pollutant, and are desirable for removal from a corporate citizenship point of view.

3 ALTERNATE BIOLOGICAL TREATMENT APPROACHES

Based on this review, several alternative approaches exist for treatment of coke plant wastewaters to achieve Best Available Technology (BAT) limits. Each alternative includes oil and tar removal, equalization and surge storage, activated sludge treatment, and solids handling. The three alternatives were:

1. No Ammonia Distillation System
2. Free Ammonia Distillation System Only
3. Free/Fixed Ammonia Distillation System

The activated sludge systems for each case would include organics removal, nitrification, and denitrification. Denitrification is included in all cases to utilize the influent wastewater organics as a carbon source to recover a portion of the oxygen and alkalinity required during nitrification, to minimize denitrification in the secondary clarification step, to optimize system operating costs, and reduce effluent nitrate levels. The size of the biological and sludge handling systems would vary depending on type of distillation system selected.

Because of concerns over potential inhibitory effects of oils, solids, and other materials, Case 1 also includes a dissolved gas flotation system prior to the activated sludge system to remove these constituents. Flow schematics of each case are presented in Figure 1.

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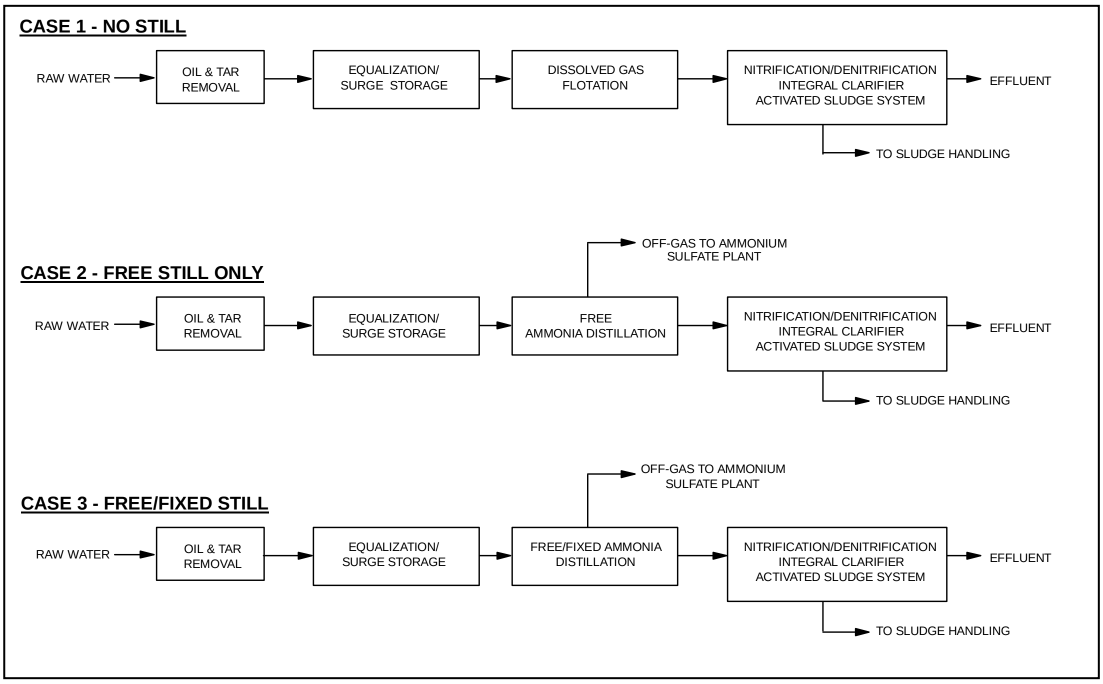

Figure 1. Cases 1, 2, and 3 flow schematic.

The activated sludge system selected for this evaluation is the relatively new and innovative ADVENT integral clarifier system referred to as the ADVENT Integral System or AIS. The system consists of a 60 degree sloped, open bottom clarifier that is installed in the biological treatment tank as shown in Figure 2.

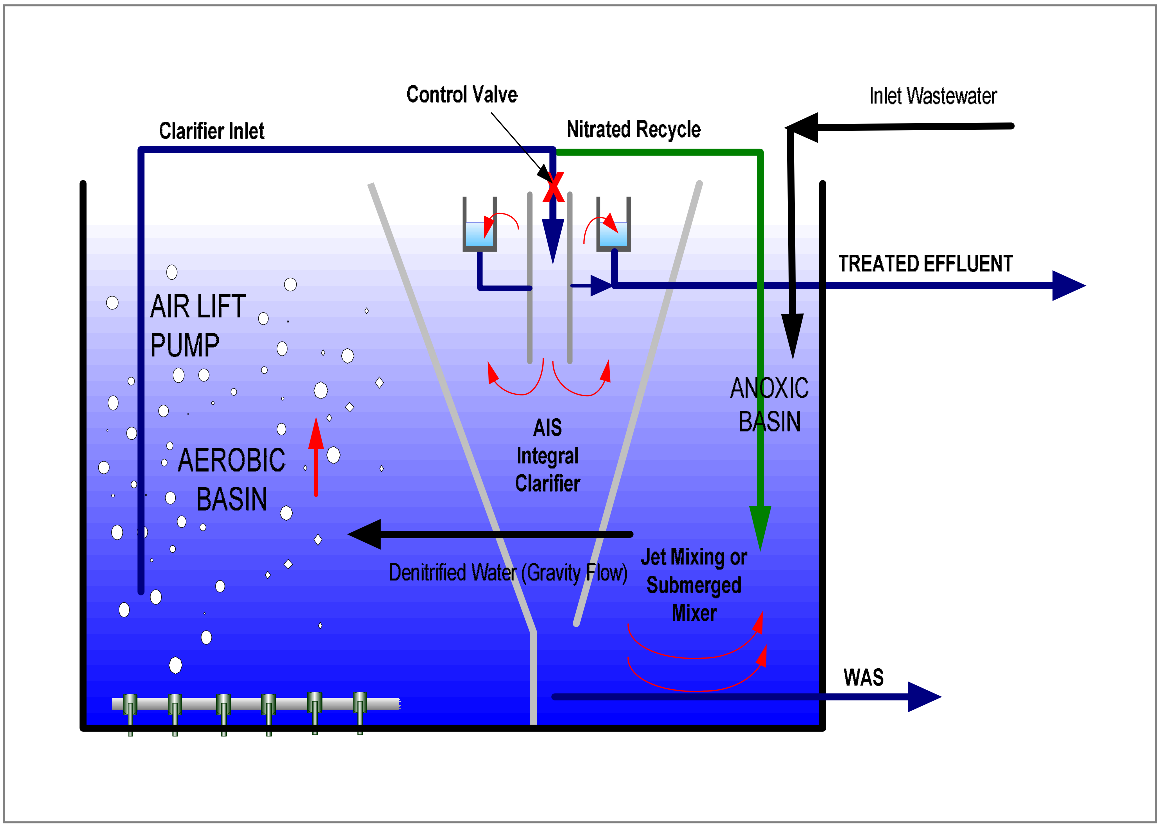

Figure 2. Advent integral activated sludge system.

In fact, the AIS clarifier separates the anoxic and aeration zones and allows nitrification, denitrification, and clarification to occur in a single tank. The inlet wastewater flows into the anoxic zone where it mixes with the return sludge from the AIS clarifier. The anoxic effluent flows through pipes under the clarifier to the aeration zone where organics are destroyed and nitrification occurs. From here, the mixed liquor is pumped with an air lift pump to the clarifier. It first passes through a static flocculator for removal of entrained air and dissolved gases. Foam can be skimmed and returned to the aeration basin. From here, the mixed liquor flows to the clarifier center well. A relatively high pumping rate is used to generate a high down-flow velocity in the clarifier. The mixed liquor flows downward into the anoxic zone through openings at the bottom of the clarifier. Due to its placement in the biological treatment basin and the fact that it utilizes no moving parts (other than the mixer in the anoxic zone), this system significantly reduces capital and operating costs, and area requirements, as compared to a conventional clarification system.

Two AIS systems are used in coke plants in Brazil, with others at coke plants in the USA, Canada, and Italy. The AIS is easy to operate since the only routine operational adjustment is for the inlet wastewater flow rate and waste sludge rate.

Typical sizing is presented for 50 m^3/hr of coke plant wastewater. Two biological treatment tanks were selected for each case. Based on our experience with coke plants and other industrial wastewaters with elevated inlet ammonia nitrogen levels, a Food-to-Microorganism (F/M) loading rate is selected based on a nitrogen-to-VSS basis. This can be compared to the conventional F/M loading rate based on BOD or COD. For coke plant wastewaters, F/M values on a kg N/kg VSS-day basis is the range of 0.015 to 0.035/day are achievable. The final design value would depend on plant specific factor such as effluent targets, operating temperatures, design MLSS/MLVSS levels selected, etc. Using mid-range values sizes were developed as shown below in Table 2:

Table 2. Coke plant biological treatment sizing comparison

Parameter	Units	No Still	Free Still Only	Free-Fixed Still
Flow	m^3/hr	50	50	50
COD	mg/L	4,000	4,000	4,000
Total N	mg/L	6,000	3,500	350
MLVSS	mg/L	6,000	6,000	6,000
Number Tanks	#	4	4	2
Anoxic/Aerobic Volume	m^3	12,000	7,000	2,800
Clarifier Overflow Rate	m/hr	0.35	0.35	0.35
Clarifier Volume	m^3	100	100	200
Tank Volume	m^3	12,100	7,100	3,000
F/M (N/VSS)	$days^{-1}$	0.025	0.025	0.025
F/M (COD/VSS)	$days^{-1}$	0.02	0.03	0.14

A nitrogen-based F/M approach was used to establish the size of the biological treatment volume and that COD-based F/M values decrease for the No Still or Free Still Only cases. Sizes would be proportionally larger for higher flow rates.

We know of 1 Free Still Only case at a coke plant, and this is located in the USA. This plant avoided the installation of a fixed still (would have been all titanium construction) and avoided upgrades to the coke oven gas handling system and ammonium sulfate recovery system for the additional ammonia load from the fixed still. Further, the plant avoided the operating costs of steam addition to the fixed still,

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and acid consumption and non-profitable generation and "sale" of ammonium sulfate fertilizer. Site specific cost factors, such as utility and chemical costs, are also critical to decisions relative to selecting the preferred approach. But it is important to know that these options are viable for new plants or for upgrades to existing plants where the features of the No Still or Free Still Only approaches may be attractive.

This system has been in continuous operation for over 10 years and consistently achieves less than 2 mg/L ammonia-nitrogen in the plant effluent. Figures 3 and 4 below show effluent ammonia and TSS data.

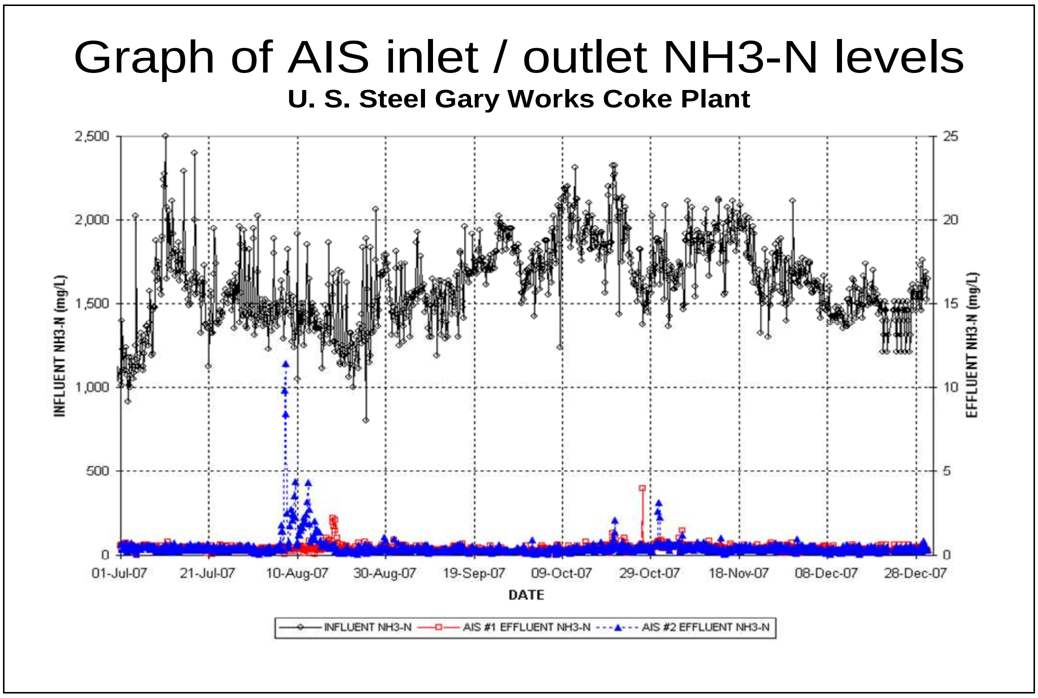

Figure 3. Coke plant AIS NH3-N performance

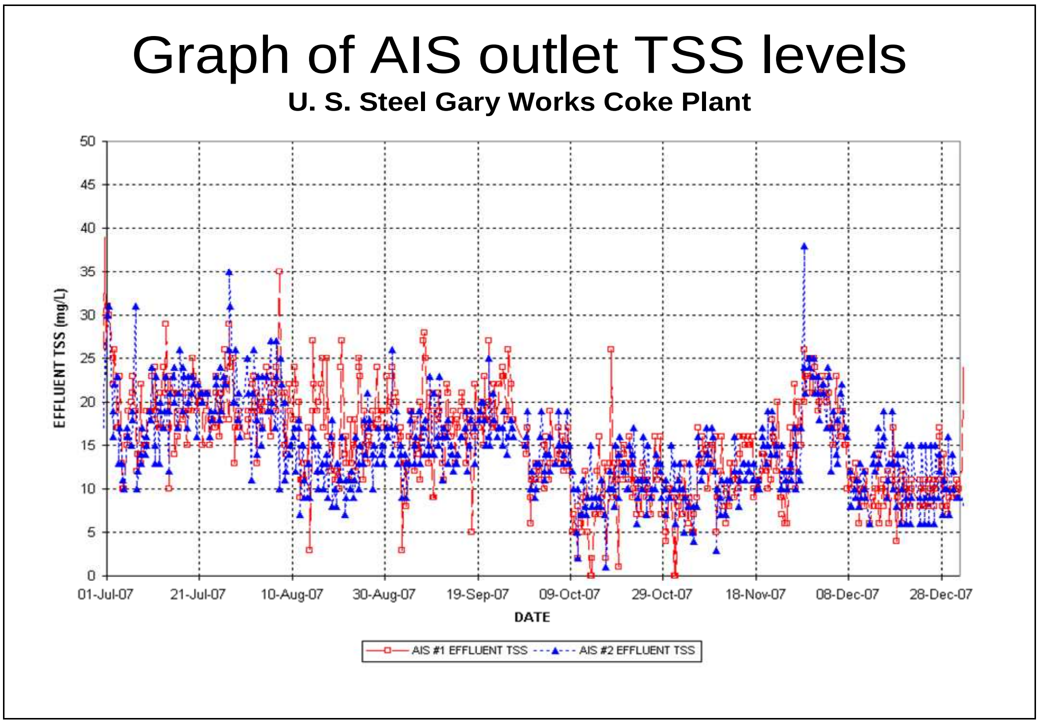

Figure 4. Coke plant AIS TSS performance.

Elsewhere, in Brazil, AIS biological treatment systems are installed and now operating in two coke plants. These systems are also days-1achieving less than 2 mg/L ammonia-nitrogen in the plant effluent. Selected photos are presented below.

Figure 5. Brazil coke plant AIS photo.

Figure 6. Brazil coke plant AIS photo.

Figure 7. Brazil coke plant AIS photo.

Figure 8. Brazil coke plant AIS photo.

4 EFFLUENT POLISHING TO ACHIEVE STRINGENT DISCHARGE LIMITS

Well designed and well operated biological treatment systems can achieve low levels of nitrogen and total phenolics, and achieve significant reductions of other compounds on coke plant wastewaters. However, additional treatment is now needed to achieve stringent effluent levels of Total Cyanide, Selenium, Mercury, Fluoride, and Poly Aromatic Hydrocarbons (PAH's), including BaP.

Cyanide is found in coke plant wastewaters of 100 mg/L or more. As mentioned before, it can readily be stripped and removed in the ammonia still system. However, due to the presence of iron and other metals, a small portion of the cyanide is bound with these metals in highly stable complexes that are not removed by stripping or biological treatment. Therefore, about 1 to 5 mg/L of metallo-complexed or "fixed" cyanide is typically found in coke plant biological system effluents. Therefore, the first effluent polishing step in this is a chemical coagulation and precipitation process to remove cyanide. It has long been known that iron salts can be used to coagulate and remove these complex cyanide compounds from coke plant wastewaters. Typically iron salts are added and mixed at the optimum pH for coagulation, and followed by polymer addition, flocculation, and solids-liquid separation. The cyanide is precipitated primarily as $Fe_4[Fe(CN)_6]_3$, a compound referred to as Prussian blue because of its characteristic blue green color. This optimum pH to precipitate the cyanide is 5.5 to 6.5 and the precipitate is then removed by settling. Effluent Total Cyanide levels of 0.5 to 1-2 mg/L can be achieved depending on inlet levels, the form of iron added, dosages, inclusion of an oxidation step, pH levels, etc. This treatment approach is shown schematically in Figure 9.

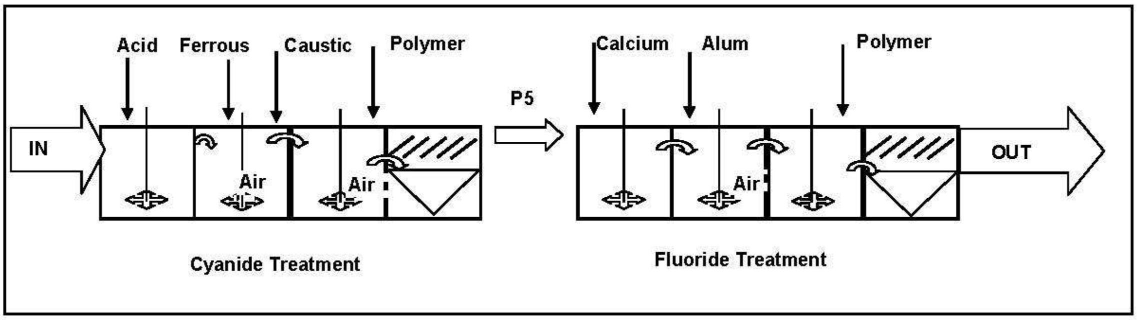

Figure 9. Coke plant effluent cyanide / fluoride removal system.

Fluoride is another parameter present in coke plant wastewaters at up to 100 mg/L that potentially is of concern from an environmental standpoint. Some countries, including Brazil, regulate its discharge concentration to no more than 10 mg/L. The most common approach for fluoride removal is precipitation with lime or calcium salts. However, the solubility of calcium fluoride is about 15 mg/L as fluoride, so this process cannot achieve the effluent limits required. Aluminum sulfate or alum is another available coagulant; however, large quantities of the aluminum fluoride precipitate are generated and settle poorly. Therefore, a combination of these two approaches was evaluated and confirmed, and then implemented at a coke plant in Brazil in 2004 to reduce fluoride to less than 10 mg/L. This step involves coagulation with calcium salts (calcium hydroxide or calcium chloride can be used) to reach the minimum fluoride solubility with calcium. This is done in a chemical mix tank with proper dosing and pH control. Then alum is added and the pH is adjusted to precipitate the soluble fluoride to less than 5 mg/L. In a third stage polymer is added for flocculation and the solids are them removed in a solids-liquid separation step. Again, effluent fluoride levels of 5 to 8 mg/L are typically achieved and the calcium salt addition provides a good settling sludge. The alum addition also provides for a very good effluent clarity and low effluent TSS levels. The system is also shown schematically in Figure 8.

However, a different but similar approach is required to meet the stringent Total Cyanide effluent limits of less than 0.1 to 0.2 mg/L. This approach was adapted from the mining industry where it was developed and was first used on coke plant wastewaters in Brazil in 2004. It involves the reduction of iron complexed cyanides to the ferrous state and then precipitation as insoluble copper-iron cyanide complexes. The first step in the revised coagulation scheme is a low pH reduction step to form the ferrous cyanide complex. Then a copper salt is added and the pH is adjusted to form the precipitate. Aeration is performed to co-precipitate the trace metals remaining in solution as hydroxide precipitates. Very low levels of Total Cyanide can be achieved and via co-precipitation the process also reduces selenium present in coke plant wastewaters to less than 50 µg/L. The copper added to complex the cyanide is also removed. Figure 10 shows this system in a schematic format.

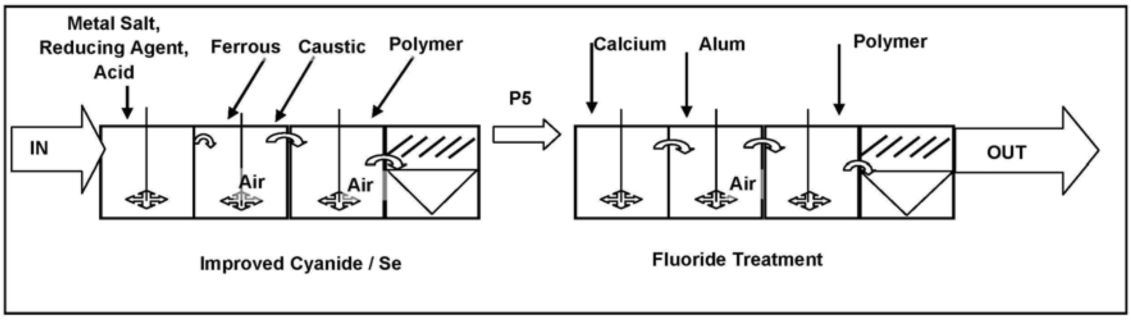

Figure 10. Coke plant effluent cyanide / selenium removal system.

A photo of a cyanide–fluoride removal system in Brazil is shown in Figure 11.

Figure 11. Photo of a brazilian coke plant cyanide / fluoride removal system.

5 ENTIRE COKE PLANT TREATMENT SYSTEM FOR LOW EFFLUENT LEVELS

In addition to reduction of Total Cyanide, Fluoride, and Selenium, at certain locations regulatory authorities require treatment to achieve low effluent levels of parameters such as COD, BaP, and PAH compounds measured as an aggregate. In these cases, effluent filters are certainly required and carbon adsorption can be used to remove organics of concern. The flow diagram show below in Figures 12 and 13 show this treatment approach now being implemented at coke plants in Canada and Italy.

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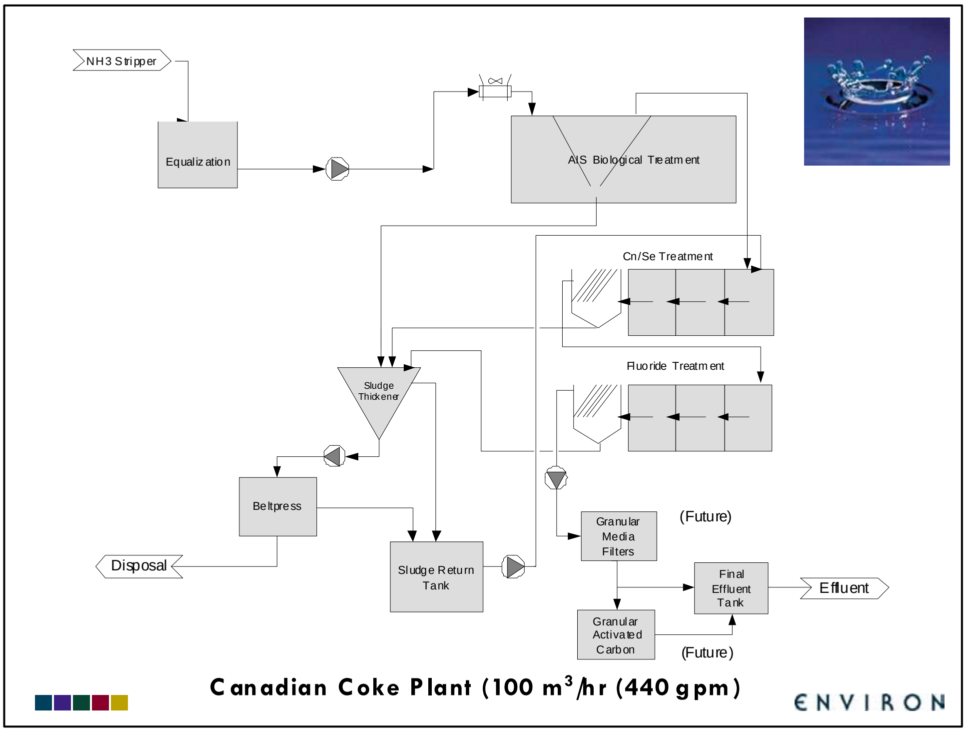

Figure 12. Flow diagram of a new canadian coke plant treatment system.

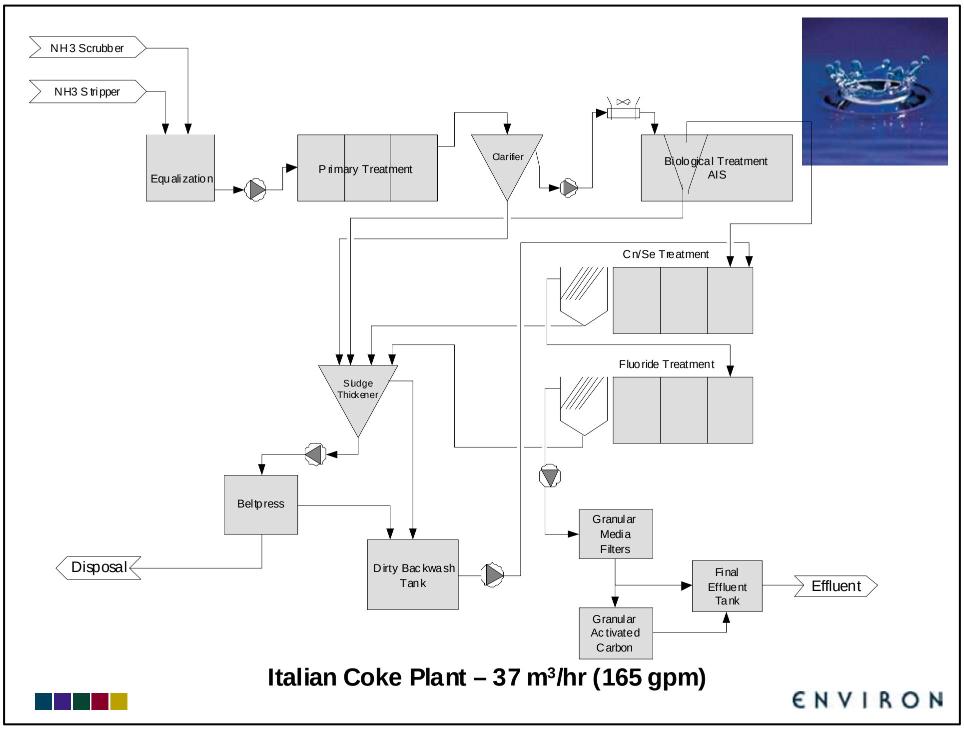

Figure 13. Flow diagram of a new italian coke plant treatment system.