A METHOD FOR PREVENTION OF ACID MINE DRAINAGE: AN UPDATE PROGRESS REPORT

Dr. Alfred H. Stiller

Department of Chemical Engineering
West Virginia University
Morgantown, WV 26506

May 3, 1983

Background

The earth-moving operations of the mining industry continually expose deeply buried minerals to weathering. Pyrite material contained in these mine spoils reacts with oxygen and water to produce sulfuric acid and solable iron salts. These compounds dissolve in water and produce acid mine drainage.

The extent of this pollution is awesome. Annually approximately 500 billion gallons of mine drainage containing 5 to 10 million tons of acid pollute over 10,000 miles of surface streams and more than 15,000 acres of impounded waters. I Methods to eliminate acid pollution can be divided into three procedures:

1. selected placement of "toxic" mine spoils which isolates these material from the environmental weathering.
2. neutralization of acid production by the addition of limestone materials. This procedure balances the excess oxidizable pyrite with an amount of basic material needed for neutralization.
3. elimination of the acid producing reaction cycle by bacteria activity or iron complexation reactions. These procedures interrupt the acid producing chain reaction described by Stumm and Morgan. [2]

The success of these treatments is confused by lack of related studies. Each technique has data which supports its effectiveness; however, the tests are normally run on different mine spoils under different conditions. This makes comparative evaluations very difficult. The mine operator does not know what to expect from these treatments; or how they eliminate the acid pollution.

The object of this research project is to study acid mine drainage production in a controlled experimental situation and to evaluate the effectiveness of a variety of treatment techniques.

Experimental Method

The experimental design carefully tests the effectiveness of the various abatement techniques against a set of controls in an idealized conditions. Acid producing material is contained in 35 gallon white plastic barrels. Each barrel is fitted with a plastic distribution plate supported above a flow plate to an exit port. Liquid flows through the material, passes through the distribution plate down the flow plate, through the exit port equipped with an air trap and collects in a sealed 5 gallon plastic can. This design insures that water flow and air flow are single directional. (See Figure 1) The particle size is less than 0.1 the diameter of the barrel which insures negligible water channeling effects. Twelve of these barrels were set up.

The acid producing material used in these experiments is cleaning plant wastes from Island Creek Coal Company's Alpine mine in Dobbin, WV. A complete characterization of the material can be seen in Table 1.

The previously described columns were each filled with three hundred pound samples of thoroughly mixed cleaning plant waste. The twelve barrels were divided into four groups of three barrels each. Of these four groups, three were treated with ameliorates and one group was used as a control. The ameliorates used. were:

1. ag lime in dosages prescribed by the Acid Base procedure (15 lb/ 300 lbs).
2. sodium laurel sulfate (2 gallons of 1% solution/300 pounds material
3. appetite rock ($Ca_5(PO_4)_3 2OH$)(2 pounds/300 pounds material)

The barrels were arranged in mixed positions so the possibility of preferential precipitation during normal weathering conditions was eliminated. Effluents from the barrels were collected 2 days after each rainfall

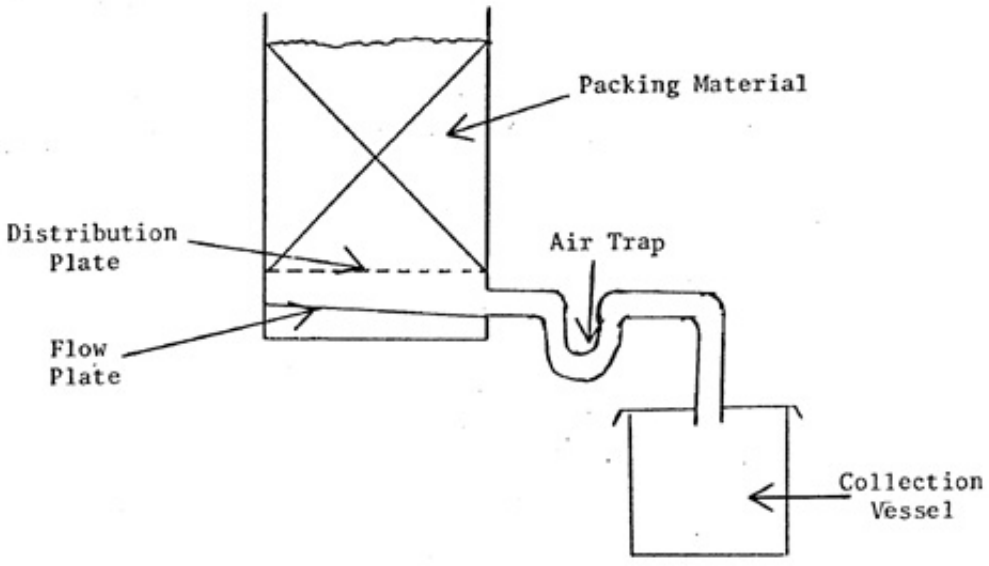

Figure 1. Experimental Design for Leaching Tanks

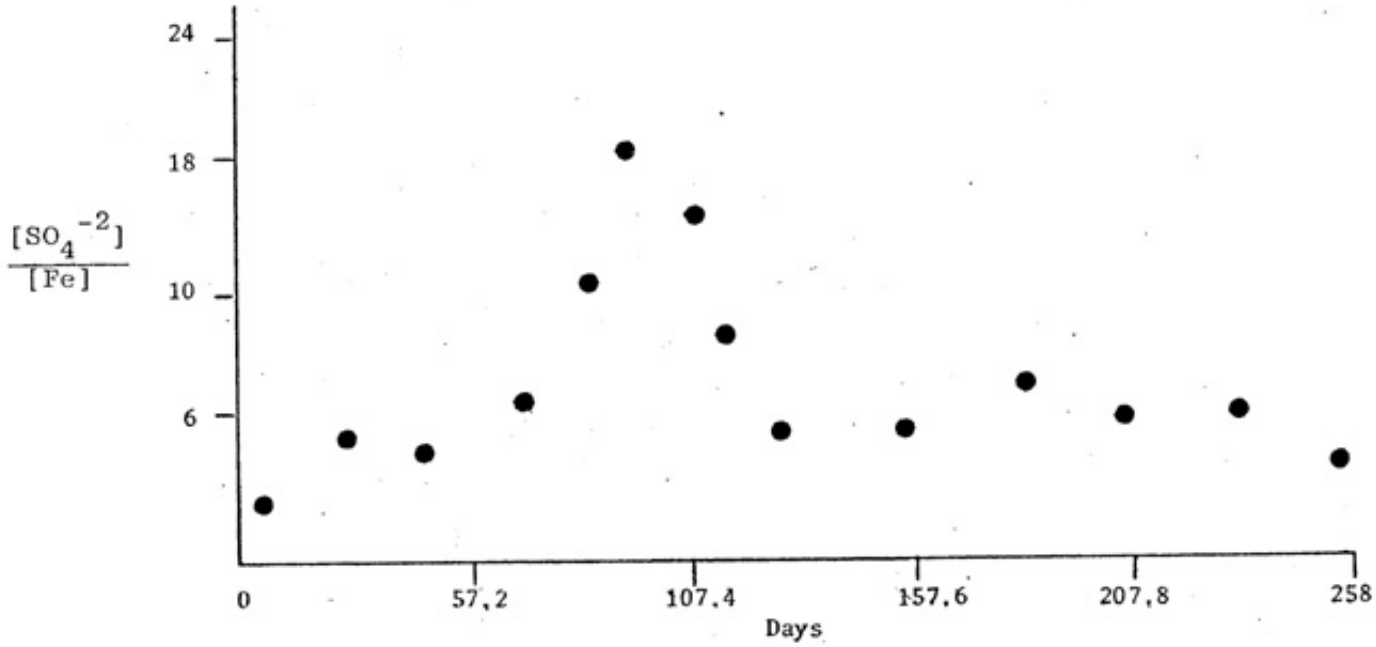

Figure 2. Sulfate to Iron Ratio versus Time

Figure 2. Sulfate to Iron Ratio versus Time

Table 1

Table 1

Analysis of Cleaning Plant Wastes

Size	Weight Percent	$CaCO_3$ equivalent (Acid Base Account) Tons/1000 Tons of Material %S	Max. From %S	Amt. Present (NP)	Max. Needed (pH 7)	Paste pH
5/8" - 1 1/2"	13.51	2.77	86.56	4.00	82.56	5.5
3/8" - 5/8"	26.81	2.88	90.00	4.79	85.21	5.2
1/4" - 3/8"	15.96	2.58	80.63	4.74	75.89	4.9
4.76 mm - 1/4"	9.04	3.27	102.19	4.00	98.19	4.7
.093" - 4.76 mm	13.19	3.54	110.63	4.49	106.14	4.6
.0116" - .093"	18.68	3.90	121.89	2.52	119.37	4.1
< .0116"	2.81	3.85	120.31	2.78	117.53	4.2

Table 2

Table 2

Ratios of Areas Under Curves for Treatment to Controls

	Cumulative Volume Dependent	Cumulative Volume Independent
$\frac{A\ PO_4}{A\ Control}$	.5931	.5165
$\frac{A\ SLS}{A\ Control}$	.7533	.6561
$\frac{A\ ag\ lime}{A\ Control}$	.8180	.4827

event and analyzed for pH, sulfate, iron, manganese, calcium, and magnesium ions. The acidity of the leachate was determined by titration with standard sodium hydroxide and the neutralization in calcium carbonate equivalents to pH: 5.5, 7, and 8.3 is recorded.

Data Interpretation

Part I - Evaluation Procedure for Abatement Techniques.

It is very difficult to analyze raw data and make a conclusive statement as to reaction consistency with time; however, we can accomplish this by comparing derived equations which fit the data. Equations can be fitted to these trends by standard computer procedures and these equations will be used to predict effects. One such procedure commonly used to test the effectiveness of treatments compares the cumulative effect of a system against the' time period of data collected. With our data this is accomplished by plotting cumulated acid contributions as indicated by sulfate concentration versus time. These data are easily computed to equations of form.

$y = m\ t^{b} + C$

A set of equations is determined for each treatment and control for the time period of data collected. By comparing the derived relationship for the treatment to the control, we can evaluate the effectiveness of the treatment. These comparisons are usually made by dividing the area under the curve for the treatment by the area under the curve for the control. The closer the number is to one, the lower the effectiveness of the treatment. Equations, correlation coefficients, and areas of the curves derived for the data can be seen in the Appendices.

Table 2 contains the ratio of the integrated areas of the treatments to the control. The effectiveness of the various treatments can be seen by comparing the ratio of the areas.

A more familiar procedure to compare abatement techniques is to determine the calcium carbonate equivalent required to neutralize the effluent stream. The procedure used in these

comparisons is the same as that used above: 1) cumulative data is plotted against time, 2) an equation is fitted to the points, 3) the equations are integrated, and 4) the ratio of the areas of the treatments to the controls are used to scale the effectiveness.. Again, the closer the ratio is to one, the lower the effectiveness of the treatment. Table 3 lists those ratios and again a similar trend is seen as indicated by the sulfate equation.

Part II - Evaluation Procedure for Testing the Acid Producing Reaction

By studying its control data, changes in the acid production reactions processes can be followed. Acid production reactions can be monitored by comparing the ratios of ion concentrations of species dependent upon pyrite oxidation. These two ions are sulfate and total iron. A simple procedure to determine this relationship is 1) to derive the cumulative equations for iron production and sulfate production and 2) subtract the consecutive points of each plot for the same time period, which produces the concentration of each ion component for that time period and divide the concentration of one ion by the other. If a single acid producing reaction dominates in acid mine drainage formation, then the ratios of these two ions contributors will be nearly constant. If more than one acid producing process is dominant the slope will not be zero. The result of this procedure can be seen in Figure 2.

Table 3

Table 3

Ratios of the Areas Under Caclite Curves Treatment to Control

	Cumulative Volume Dependent	Cumulative Volume Independent
$\frac{A\ PO_4^{-3}}{A\ Control}$	.5156	.5928
$\frac{A\ SLS}{A\ Control}$	.7176	.6696
$\frac{A\ ag\ lime}{A\ Control}$	.1645	.6944

Results

There are no conclusions in this. report because as noted the work is still in progress; however, several hypotheses can be drawn from the interpreted data.

First, as the plot of the ratio of $[SO_4^{-2}]/[Fe]$ demonstrates; more than one chemical process is responsible for acid production. The Plot would be linear with zero slope if a single process were responsible for acid production. The appearance of an apex shows that at least one other process which produces high concentrations of soluble sulfate compared to soluble iron is occurring. This phenomena took place in late September and early October. Since reaction products leach from the barrel about a month after the reaction, it is probable that this disproportionate sulfate/iron reaction takes place in August. Because there were several high temperature days with moderate rainfall during August, it is hypothesized that the second

reaction is a low energy combustion of pyrite. (Data used to determine the temperature dependence on the reaction rate for pyrite calculation show us similar phenomena.) If this is true, it is possible to eliminate this reaction by keeping the surface of pyrite containing material cool. This can be accomplished by deep burial of toxic material as suggested by the task force recommendations.

Second, comparisons of the effectiveness of the various treatments can be seen by reading the ratios of areas under the derived curve portions describing the cumulative sulfate concentration eluted from the barrels. (See Table 2) As can be seen, the ratios can be ranked from least effective to most effective:

1. Ag lime
2. SLS
3. Phosphate

(Note, these are results of incomplete studies and are being reported as an update on progress on these studies, not as conclusions.) The sulfate equations results are duplicated by the calcium carbonate equivalent equations.

There is one particularly with the ag lime data that merits discussion: the discrepancy between the areas under the cumulative volume dependent equation and the volume independent equation. . It appears that the volume flow from the ag lime samples is about 60% that of the control and other test samples. The decrease in volume will be reflected in the cumulative volume independent equations, but not in the cumulative Volume dependent equations. This difference may be due to the hydration of iron oxides which are seen in the bed material or in the formation of calcium sulfate hydrate crystals. In no way is this due to flooding of the ag lime samples. The cumulative volume dependent sulfate equations and the limestone equivalent equations show that the ag lime treatment is not as effective in improving water quality as the other treatments. So, any improvement of the water reservoir from ag lime treatment is due to decreased volume of the elutent, not to chemical improvement of the water quality. This is in agreement with a recent EPA report. [3]

References

1. U.S. Department of the Interior, "Mine Drainage Pollution Control Research and Development Pro3ects,11 Federal Water Pollution Control Administration, 1968.
2. Strumm, W. and Morgan, J.J., "Aquatic Chemistry-An Introduction Emphasizing Chemical. Equilibrium in Natural Waters," Wiley, NY: NY, (1970).
3. U.S. Environmental Protection Agency, "Leachability and Revegetation of Solid Waste from Mining," Project Summary, EPA-600/S2-82-093, March 1983.

APPENDIX A

Volume Dependent Cumulative Function for Sulfur

APPENDIX A

Volume Dependent Cumulative Function for Sulfur

$$y = m\,t^{b} + c$$

$$y = \frac{\Sigma[SO_4][ml]}{\Sigma\ ml}$$

			R	Area
Sample	1	$61{,}030.6406\ t^{.3406} - 22{,}457.5625$	.9764	25,181,697
	2	$51{,}488.0781\ t^{.3689} - 19{,}471.8750$	.9788	24,040,508
	3	$70{,}353.0000\ t^{.3175} - 23{,}136.0000$	.9742	26,492,450
	10	$90{,}193.6250\ t^{.3744} - 40{,}716.1250$	.9784	42,370,456
	11	$103{,}385.2500\ t^{.3412} - 41{,}612.3750$	.9756	42,347,538
	12	$85{,}030.6875\ t^{.3912} - 39{,}727.1875$	.9803	42,936,029
Sample	4	$73{,}551.2500\ t^{.5410} - 47{,}222.5000$	.9930	227,621,557
	5	$75{,}054.6875\ t^{.5204} - 57{,}798.0000$	.9913	206,502,918
	6	$80{,}430.8750\ t^{.4964} - 58{,}669.9375$	.9907	196,000,806
	10	$85{,}316.9375\ t^{.5667} - 196{,}749.937$	.9856	265,570,802
	11	$134{,}565.375\ t^{.5456} - 231{,}926.000$	.9816	389,867,561
	12	$74{,}051.4375\ t^{.6001} - 119{,}061.687$	.9899	292,077,765
Sample	7	$237{,}561.000\ t^{.2674} - 8{,}024.0000$	.9890	147,001,729
	8	$64{,}050.7617\ t^{.5934} - 47{,}391.7500$	.9899	186,763,590
	9	$198{,}245.687\ t^{.3600} - 122{,}037.687$	.9624	164,698,482
	10	$160{,}116.187\ t^{.4303} - 93{,}423.8750$	.9775	191,389,515
	11	$181{,}314.062\ t^{.4928} - 122{,}720.000$	.9829	292,174,082
	12	$176{,}129.625\ t^{.4308} - 83{,}159.0000$	.9815	214,842,222

APPENDIX B

Volume Independent Cumulative Functions for Sulfate

APPENDIX B

Volume Independent Cumulative Functions for Sulfate

$$y = m\,t^{b} + c$$

$$y = \Sigma[SO_4][ml]$$

			R	Area
Sample	1	$399{,}643.812\ t^{.1780} + 33{,}790.6875$	.9908	99,127,853
	2	$213{,}649.562\ t^{.3355} + 206{,}952.062$	.9178	120,143,684
	3	$396{,}048.062\ t^{.1983} + 39{,}153.9375$	.9907	106,837,502
	10	$389{,}962.750\ t^{.3645} + 214{,}397.000$	.9795	221,605,253
	11	$818{,}856.812\ t^{.1814} + 15{,}426.0000$	.9988	199,366,336
	12	$772{,}043.062\ t^{.2569} + 271{,}596.000$	.9650	283,858,429
Sample	4	$126{,}713.375\ t^{.3673} + 59{,}326.8750$	.9845	376,243,249
	5	$113{,}306.000\ t^{.3431} - 1{,}942.5625$	.9874	290,094,499
	6	$113{,}371.000\ t^{.3727} - 18{,}589.3125$	.9812	311,674,579
	10	$112{,}606.875\ t^{.4907} - 112{,}877.437$	.974	388,741,397
	11	$106{,}268.562\ t^{.5002} - 92{,}711.8125$	.9770	525,413,773
	12	$34{,}806.8594\ t^{.6589} + 28{,}056.0625$	.978	369,379,435
Sample	7	$65{,}328.2070\ t^{.5854} + 83{,}830.5000$	.975	190,737,481
	8	$11{,}382.5430\ t^{.9945} + 1{,}137{,}621.00$	.7904	428,208,711
	9	$903{,}022.125\ t^{.2186} - 27{,}654.0000$	.984	448,650,488
	10	$850{,}087.687\ t^{.3646} - 21{,}968.0000$	.9816	820,020,686
	11	$994{,}451.687\ t^{.4132} + 772{,}261.000$	.9349	1,351,996,135
	12	$1{,}281{,}551.0\ t^{.3246} - 89{,}914.0000$	.9777	1,019,382,676

APPENDIX C

Volume Dependent Cumulative Functions for $CaCO_3$

APPENDIX C

Volume Dependent Cumulative Functions for $CaCO_3$

$$y = m\,t^{b} + c$$

$$y = \frac{\Sigma[CaCO_3][ml]}{\Sigma\ ml}$$

			R	Area
Sample	1	$62,414.5\ t^{.3118} - 20,658.8$	.9743	22,897.118
	2	$49,402.9\ t^{.3304} - 16,749.9$	.9762	19,642,324
	3	$62,842.7\ t^{.2892} - 18,045.8$	.9725	21,160,694
	10	$79,003.6\ t^{.3549} - 33,610.6$	.9766	34,208,843
	11	$89,686.7\ t^{.3287} - 34,328.7$	.9746	34,923,307
	12	$75,284.9\ t^{.3919} - 33,511.9$	.9807	38,333,241
Sample	4	$27,476.3\ t^{.5931} - 9,046.8$	.9947	34,439,508
	5	$30,748.0\ t^{.5588} - 16,460.4$	.9941	32,381.570
	6	$29,170.3\ t^{.5925} + 17,627.7$	.9942	39,573,018
	10	$36,042.9\ t^{.6190} - 90,722.5$	.9889	40,929,066
	11	$61,497.2\ t^{.5816} - 75,964.2$	.9915	66,463.945
	12	$36,863.8\ t^{.6346} - 41,499.9$	.9931	51,509,023
Sample	7	$121,291.4\ t^{.2508} - 112.1$	.9843	38,551,486
	8	$38,412.0\ t^{.4153} - 25,510.7$	.9733	20,721,017
	9	$94,950.0\ t^{.3293} - 63,695.1$	.9406	33,818,240
	10	$109,015.1\ t^{.3829} - 56,841.1$	.9660	52,312,646
	11	$189,611.1\ t^{.3452} - 65,472.7$	.9713	80,374,059
	12	$104,905.4\ t^{.3935} - 61,620.0$	.9623	51,906,251

APPENDIX D

Volume Independent Cumulative Function for $CaCO_3$

APPENDIX D

Volume Independent Cumulative Function for $CaCO_3$

$$y = m\,t^{b} + c$$

$$y = \Sigma[CaCO_3][ml]$$

			R	Area
Sample	1	$415{,}665.3\ t^{.1443} - 3{,}488.3$	.9801	86,199,955
	2	$209{,}478.3\ t^{.2898} + 124{,}738.0$	.9344	92,726,330
	3	$359{,}139.2\ t^{.1606} + 6{,}268.2$	.9808	80,544,862
	10	$345{,}401.6\ t^{.3420} + 132{,}901.0$	.9847	174,351,465
	11	$714{,}791.4\ t^{.1661} - 9{,}817.0$	.9937	161,139,691
	12	$680{,}677.8\ t^{.2531} + 275{,}908.0$	.9511	251,256,457
Sample	4	$274{,}069.5\ t^{.4195} + 119{,}769.0$	.9866	186,692,147
	5	$250{,}543.0\ t^{.4012} - 5{,}681.0$	.9927	145,609,160
	6	$288{,}181.7\ t^{.3996} + 191{,}994.0$	.9865	190,014,050
	10	$294{,}295.6\ t^{.5149} - 466{,}930.0$	.9797	218,400,933
	11	$262{,}263.8\ t^{.5676} - 136{,}516.0$	.9781	287,439,281
	12	$85{,}435.1\ t^{.7544} + 47{,}943.0$	.9809	222,039,596
Sample	7	$35{,}323.2\ t^{.5141} - 330.2$	.9923	41,998,039
	8	$7{,}865.0\ t^{.8800} + 129{,}889.2$	.9526	49,485,397
	9	$436{,}260.7\ t^{.2201} - 144{,}712.5$	.9252	105,493,777
	10	$586{,}532.2\ t^{.3297} - 219{,}926.0$	.9691	229,969,296
	11	$1{,}093{,}081.0\ t^{.2488} - 136{,}314.0$	.9849	328,556,838
	12	$729{,}375.6\ t^{.3268} - 327{,}612.0$	.9458	275,822,151

APPENDIX E

Volume Dependent Cumulative Function for Total Iron

APPENDIX E

Volume Dependent Cumulative Function for Total Iron

$$y = m\,t^{b} + c$$

$$y = \frac{\Sigma[Fe][ml]}{\Sigma\ ml}$$

			R	Area
Sample	1	$19{,}799.17\ t^{.2954} - 5{,}924.43$	.9727	6,823,930
	2	$19{,}779.02\ t^{.2939} - 5{,}728.75$	.9725	6,794,283
	3	$17{,}990.21\ t^{.2891} - 5{,}073.55$	.9722	6,066,071
	10	$29{,}406.79\ t^{.3134} - 10{,}228.81$	.9729	10,806,503
	11	$32{,}986.96\ t^{.3136} - 11{,}099.44$	.9739	12,177,633
	12	$4{,}530.28\ t^{.6067} - 595.09$	.9869	6,103,837
Sample	4	$12{,}590.77\ t^{.5604} - 280.19$	.9951	14,122,098
	5	$13{,}859.73\ t^{.5165} - 5{,}038.40$	.9941	12,392,701
	6	$12{,}883.47\ t^{.5211} - 5{,}884.00$	.9937	11,608,698
	10	$13{,}537.53\ t^{.6171} - 30{,}151.75$	.9900	15,680,887
	11	$24{,}199.10\ t^{.5218} - 21{,}318.63$	.9907	20,649,940
	12	$14{,}484.17\ t^{.5748} - 7{,}434.81$	.9938	16,402,745
Sample	7	$34{,}035.49\ t^{.2566} - 255.00$	.9828	11,045,410
	8	$12{,}875.26\ t^{.3760} - 8{,}359.55$	.9632	5,789,314
	9	$40{,}394.49\ t^{.3168} - 24{,}072.31$	.9438	13,879.936
	10	$39{,}976.35\ t^{.3680} - 16{,}816.06$	.9709	18,388,783
	11	$29{,}125.32\ t^{.4262} - 19{,}060.75$	.9698	16,566,001
	12	$32{,}416.35\ t^{.3597} - 12{,}024.81$	.9687	14,555,125

APPENDIX F

Volume Independent Cumulative Function for Total Iron

APPENDIX F

Volume Independent Cumulative Function for Total Iron

$$y = m\,t^{b} + c$$

$$y = \Sigma[Fe][ml]$$

			R	Area
Sample	1	$129{,}926.94\ t^{.1093} + 5{,}007.69$	.9862	24,197,220
	2	$83{,}076.06\ t^{.2302} + 40{,}624.19$	.9073	29,162,204
	3	$101{,}503.56\ t^{.1528} + 7{,}143.69$	.9837	22,720,791
	10	$127{,}336.25\ t^{.2748} + 41{,}965.25$	.9748	49,567,506
	11	$259{,}113.56\ t^{.1304} + 14{,}810.81$	.9897	52,886,105
	12	$38{,}367.20\ t^{.4867} + 128{,}592.94$	.8613	47,108,133
Sample	4	$126{,}713{,}38\ t^{.3673} + 59{,}326.88$	.9845	71,506,362
	5	$113{,}306.00\ t^{.3431} - 1{,}942.56$	.9874	52,007,504
	6	$113{,}371.00\ t^{.3727} - 18{,}489.31$	.9812	56,727,896
	10	$112{,}606.88\ t^{.4907} - 112{,}877.44$	.9742	81,467,228
	11	$106{,}268.56\ t^{.5002} - 91{,}711.81$	.9770	82,102,346
	12	$34{,}806.86\ t^{.6589} + 28{,}056.06$	.9783	62,337.580
Sample	7	$9{,}738.61\ t^{.5847} + 1{,}860.94$	.9868	12,333,235
	8	$2{,}573.69\ t^{.8439} + 32{,}212.56$	.9422	13,351.546
	9	$183{,}303.06\ t^{.1889} - 37{,}499.31$	.9376	41,088,326
	10	$216{,}981.31\ t^{.2930} - 48{,}838.60$	.9737	75,905,535
	11	$161{,}452.19\ t^{.3637} - 5{,}088.25$	.9786	80,317,062
	12	$239{,}625.88\ t^{.2573} - 76{,}234.88$	.9238	69,244,425