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TECHNICAL

BULLETIN NO.35

DÉPARTMENT OF ENERGY, MINES AND RESOURCES

Precipitation of Heavy Metals from Natural and Synthetic Acidic Aqueous Solutions during Neutralization with Limestone

R.O.VAN EVERDINGEN and J.A.BANNER

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INLAND WATERS BRANCH DEPARTMENT OF ENERGY, MINES AND RESOURCES OTTAWA, CANADA, 1971

CONTENTS

																						Page
Abstract			•	•	•	•	•	•	•	•	•	•	•		•		•		•			v
Introduction	•	•	•		¥	•	•	•	•	•	÷	• ·		•	•		•			•	•	1
Description of the equipment	5.		•	•:	•	•	•			•	•			•		•	•	•	•	•	•	2
Testing procedures		.•	÷					•	•		÷					÷			÷		•	2
Natural acidic waters .	•	•	•	٠	•	•	•	•	•	•	•	•	•	•	•	•						. 2
Synthetic acidic waters	•	۲.	•	•	٠	•	·	•	•	•	•	•	•	•	•	•	•	•	•	•	•	4
Discussion of results																						
Natural acidic waters .																						
Synthetic acidic waters																						
Conclusions				•																		
References	•	•	•	•	•	•	٠	•	•	•	۲	•	•	•	•	•	•	•	•	•	•	8

TABLËŠ

Table I.	Results of limestone neutralization tests on water from the Paint Pots Springs, Kootenay National Park, British	
	Columbia	્.3
Table II.	intereste de l'emperente interestate de la construction de synthetic	
	acidic water	5

ILLUSTRATIONS

	Equipment used in limestone neutralization test . frontispiece
Figure 1.	pH vs time for acidic spring water (tests I to IV)
Figure 2a.	pH vs Eh for synthetic acidic water (test 1) 10
Figure 2b.	pH and Eh vs time for synthetic acidic water (test 1) 11
Figure 3a.	pH vs Eh for synthetic acidic water (test 2) 12
Figure 3b.	pH and Eh vs time for synthetic acidic water (test 2) 13
Figure 4a.	pH vs Eh for synthetic acidic water (test 3)
Figure 4b.	pH and Eh vs time for synthetic acidic water (test 3) 15
Figure 5a.	pH vs Eh for synthetic acidic water (test 4) 16
Figure 5b.	pH and Eh vs time for synthetic acidic water (test 4) 17
Figure 6a.	pH vs Eh for synthetic acidic water (test 5)
Figure 6b.	pH and Eh vs time for synthetic acidic water (test 5) 19
Figure 7a.	pH vs Eh for synthetic acidic water (test 6) 20
Figure 7b.	pH and Eh vs time for synthetic acidic water (test 6) 21
	· · · · · · · · · · · · · · · · · · ·

ABSTRACT

Iron, aluminum, manganese, copper, lead and zinc in natural and synthetic acidic water with H⁺ concentrations ranging from 4.0 x 10^{-3} to 6.3 x 10^{-4} were circulated through crushed limestone. This resulted in neutralization of the acidity and removal of up to 99.9% of the dissolved Fe, 96.6% of Al, 35 to 52% of Mn, 99.8% of Cu, 99.9% of Pb and 97.1% of Zn. Minimum metal concentrations obtained were (in ppm): 0.05 Fe⁺⁺, <0.3 Al⁺⁺⁺, 0.22 Mn⁺⁺, 0.006 Cu⁺⁺, 0.002 Pb⁺⁺ and 3.7 Zn⁺⁺. Intensive aeration accelerated the process, both by increasing the rate of oxidation from Fe⁺⁺ to Fe⁺⁺⁺, and by removal of dissolved carbon dioxide generated by solution of the limestone.

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INTRODUCTION

A simple test of neutralization with limestone, applied to samples of acidic heavy-metal bearing water (pH ranging from 2.8 to 3.6) from the Paint Pots Springs in Kootenay National Park, British Columbia, indicated that most of the dissolved iron, much of the dissolved lead and zinc, and some of the dissolved copper and manganese could be precipitated by this method (van Everdingen, 1970). The limestone neutralization process has been applied elsewhere to neutralize acidic coal-mine drainage, simultaneously achieving almost complete removal of dissolved iron from the water. Extensive research in the United States has concentrated on these particular aspects of the process; specific projects were aimed at determining optimum grain sizes, mixing ratios and residence times, as well as improving the settling characteristics of the resulting mixed iron-hydroxide and calcium-sulfate sludge (Mihok *et al.*, 1968).

Relatively little is known so far about the behaviour of other heavy-metal ions in an acidic water that is being subjected to limestone neutralization. Some of these ions occur in appreciable concentrations in drainage from dumps and settling ponds at some sulphide ore mines (Schmidt and Conn, 1969). These ions are harmful to aquatic life (especially fish), even in low concentrations. It was thought useful, therefore, to carry out some further tests to determine to what extent the ions of Fe, Al, Mn, Cu, Pb and Zn could be expected to be precipitated from an acidic water neutralized by circulation through crushed limestone.

Initial tests were carried out on natural spring water obtained from the Paint Pots Springs; further tests made use of synthetic acidic water produced in the laboratory. The results of these tests, given later in this report, indicate the reduction of heavy-metal concentrations for aqueous solutions that contain only the completely oxidized sulfur species (sulfate ion), as well as a high concentration of dissolved iron. No attempt was made to assess the influence of partially reduced sulfur compounds (such as thiosulfate, trithionate, etc.) and low dissolved-iron concentrations, both of which seem to characterize the early stages of drainage from sulfidemine tailings and settling ponds (Schmidt and Conn, 1969). In these cases, most of the acid generation presumably results from oxidation, and subsequent hydrolysis, of the partially reduced sulfur species. It is possible that the combination of aeration and neutralization will have similar effects on the dissolved heavy metals in these cases as in the case of acidic water with high Fe⁺⁺ and sulfate contents. The presence of sulfur-oxidizing bacteria should have an accelerating effect on the reactions.

DESCRIPTION OF THE EQUIPMENT

The equipment used for the neutralization tests is shown in the frontispiece photograph. It consisted of a 1.6-liter glass reservoir (1) with a glass cover (2). The solution to be treated was pumped from the reservoir by a Faller model 680 vibrator pump (3) into the reaction column (4). The column was made of glass tubing with an outside diameter of 3 cm (I.D. 2.8 cm), 33 cm long, and filled to a height of 25 cm with crushed limestone (>97% CaCO₃). A 0.5-cm thick mat of glass fibers was placed below the limestone to prevent the limestone from falling into the pump. A return line (5) returned the water to the reservoir; it was also used for the filling of sample bottles at the end of each test.

The pH of the solution was measured with a Sargent model S-30072-15 combination electrode (6), inserted in the top of the reaction column; the pH was recorded, via a Corning model 6 pH meter (7), on one channel of a Hewlett-Packard model 7100B dual-channel millivolt recorder (8). The redox potential (Eh) of the solution was measured in the reservoir with a Fisher model 13-639-102 platinum electrode and a Fisher model 13-639-52 reference electrode (9); using a 10x attenuator to raise the recorder's input impedance to 10 megohms, the Eh was recorded on the second channel of the recorder. During the tests on spring water, only the pH was recorded because a dualchannel recorder was not available at the time.

Also shown in the photograph is the power supply (10) that supplied 12 volts, alternating current, 60 Hz, for the operation of the pump, and 25 volts, alternating current, for the initial priming.

TESTING PROCEDURES

Natural acidic waters: In the tests on natural acidic water, 1500 cc of the water were treated each time. The water, obtained from the Paint Pots Springs on the day preceding the first test, was stored in tightly capped glass bottles. The second column of Table I shows the concentrations of the essential constituents of the spring water at the start of the first test. Before the start of the other tests, the pH, oxygen content and dissolvediron content of the water were again determined; the oxygen content was zero in all water samples; the pre-test pH and the Fe⁺⁺ content are given in parentheses in the columns for tests II, III and IV in Table I. It can be seen that a gradual decrease in the iron content of the untreated water is accompanied by a slow drop in pH. Redox potentials were not recorded during these tests.

During Tests I and II, the water was circulated through crushed limestone having particles sizes between 2 and 4 mm. The same batch of limestone was used for both tests. During Tests III and IV, the limestone particles used ranged in size from 0.8 to 2.0 mm. The rate of flow through the column was such that some "lifting" of the smaller limestone particles occurred during the latter two tests.

Samples of the water resulting from Tests I - IV were analyzed for Ca^{++} , Fe^{++} , Mn^{++} , Cu^{++} , Pb^{++} , Zn^{++} , HCO_3 , SO_4 , CI^- , dissolved oxygen, and pH. Results of these analyses are given in Table I. Figure 1 illustrates the changes in pH with time during these tests.

					· · · · · · · · · · · · · · · · · · ·	
Constituents	Original	÷				
consciences	Spring Water	I	II	III	IV	
Ca ⁺⁺ *	137.	432.	418.	436.	404.	
Mg ⁺⁺	61.9	. —	-	-	-	
Fe ⁺⁺	300.	<0.05	<0.05 (from 225)	0.05 (from 175)	0.11 (from 135)	
Mn ⁺⁺	0.46	0.29	0.34	0.38	0.22	
Cu ⁺⁺	0.017	0.013	0.012	0.008	0.014	
Pb ⁺⁺	0.15	<0.010	<0.010	<0.010	<0.010	
Zn ⁺⁺	52.	5.1	7.4	8.6	3.7	
нсо_3	350.	152.	110.	372.	183.	
$so_{4}^{= **}$	1190.	1100.	1100.	960.	1025.	
C1 ⁻ ***	1.5	35.	50.	35.	35.	
0 ₂	0.0	7.2	6.2	3.4	6.6	
рН	3.60	7.39	7.13 (from 3.15)	7.08 (from 3.08)	7.53 (from 2.77)	
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Results of Limestone Neutralization Tests on Water from the Paint Pots Springs (concentrations in ppm)

* Increase in Ca⁺⁺ from solution of limestone

** Decrease in $SO_4^{=}$ from precipitation of CaSO₄

*** Increase in C1 resulting from KC1 leakage from reference electrode

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TABLE I

Synthetic acidic waters: The synthetic acidic water used in the remaining tests was produced in the laboratory in 2-liter batches. Reagentgrade chemicals were used; 200 mg Al₂(SO₄)₃.18H₂O, 4400 mg FeSO₄.7H₂O, 1320 mg MgSO₄.7H₂O, and 1540 mg ZnSO₄.7H₂O were weighed to the nearest 1 mg; 40 mg CuSO₄.5H₂O, 50 mg MnSO₄.H₂O and 20 mg PbSO₄ were weighed to the nearest 0.1 mg. The chemicals were added to 1 liter of double-distilled water which was being stirred in a 2.5-liter beaker, in the following order: Al, Pb, Zn, Mn, Cu, Mg, Fe. During this time the pH dropped to 4.40. Then another liter of double-distilled water, and 2 drops of concentrated H₂SO₄ to lower the pH to about 3.4, were added to the solution. The only salt that did not dissolve properly under these conditions was PbSO₄; only 3 - 3.5 ppm of lead were detected in the analyses, although the quantity applied should have resulted in a lead concentration of the order of 6.5 ppm. The original heavy-metal concentrations in each of the batches of synthetic water are listed as analyses 'A' in Table II.

The conditions during the treatment tests were varied, as follows:

- Test 1: 1.5 liters, circulated through crushed limestone (size 2 4 mm) immediately after preparation of the solution; no contact with air, except in the glass reservoir.
- Test 2: 1.5 liters, circulated through crushed limestone (size 2 4 mm) 48 hours after preparation of the solution; no air contact except in the glass reservoir.

Test 3: 1.5 liters, circulated through crushed limestone (size 2 - 4 mm) immediately after preparation of the solution; air bubbles were entering through the pH-electrode plug.

- Test 4: 1.5 liters, circulated through crushed limestone (size 2 4 mm) immediately after preparation of the solution; air was bubbled through the solution in the reservoir by means of a submerged porous ceramic cup connected to a compressed-air supply.
- Test 5: 1.5 liters, mixed with an excess of reagent-grade CaCO₃ powder, stirred and aerated.
- Test 6: 0.5 liter, mixed with an excess of reagent-grade $CaCO_3$ powder, stirred and aerated 19 hours after preparation of the solution.
- Test 7: 1.5 liters, circulated through crushed tempered glass (particle size 2 - 4 mm) to check on the influence of circulation in the absence of reactive material in the column.

Both pH and Eh were recorded during these tests (Figs. 2 - 7). Samples of the water produced by each of the tests were analysed for Ca⁺⁺, Fe⁺⁺, A1⁺⁺⁺, Mn⁺⁺, Cu⁺⁺, Pb⁺⁺, Zn⁺⁺, pH and Eh; results of these analyses are presented in Table II.

DISCUSSION OF RESULTS

Natural acidic waters: The results of the tests on spring water (Fig. 1) show, in the first six minutes, a rapid increase in the pH to values between 5.0 and 5.6, followed by a relatively slow further increase to values about 6.7, followed by a further increase to values between 7.0 and 7.6; the latter figure was reached more rapidly in tests 1 and 4. Run

TABLE II

·									
Number		рН	Eh,						
	Ca ⁺⁺	Fe ⁺⁺	A1 ⁺⁺⁺	Mn ⁺⁺	Cu ⁺⁺	Pb ⁺⁺	Zn ⁺⁺		m volt.
A 1 -	0.0	470.	8.8	7.8	4.9	3.3	176.	3.38	+579
B	559.	0.9	<0.3	6.2	0.015	0.003	17.	• 7.87	+445
A 2 -	0.0	465.	8.6	7.6	4.9	3.4	175.	3.12	+592
B	544.	0.8	<0.3	5.9	0.017	0.003	12.	7.52	+487
A 3 -	0.0	470.	8.7	7.9	4.9	-3.3	174.	3.41	+574
B	498.	1.0	<0.3	6.3	0.011	0.002	26.	7.51	+474
A _	0.0	460.	8.5	7.5	4.9	3.5	178.	3.43	+585
В	484.	0.9	<0.3	5.6	0.006	0.003	12.	8.01	+465
A 5 -	0.0	470.	8.7	7.0	5.1	3.4	176.	3.48	+558
В	491.	1.3	<0.3	5.2	0.013	0.004	8.5	7.93	+454
A 6 -	0.0	465.	8.7	7.0	5.1	3.4	176.	3.52	+584
В	495.	0.6	<0.3	4.5	0.012	<0.002	5.0	7.96	+472
A 7 -	0.0	480.	9.7	8.0	5.1	3.0	182.	3.45	+563
В	0.0	460.	9.2	7.8	4.8	2.9	170.	3.07	+557

Results of Limestone Neutralization Tests on Synthetic Acidic Water

A = original mixture; B = treated as follows:

1B - 1.5 liters, through limestone, no air leakage

2B - 1.5 liters, through limestone, after 2 days of "ageing", no air leakage
3B - 1.5 liters, through limestone, air bubbles entering at plug on top of column
4B - 1.5 liters, through limestone, with forced aeration
5B - 1.5 liters, in beaker with CaCO₃ powder, stirred and aerated
6B = 0.5 liter, same as (5), but after 19 hours of "ageing"
7B - 1.5 liters, through crushed tempered glass

times varied from 23 to 69 hours. The pH values after 10 hours were 6.50, 6.68, 6.70 and 7.09, respectively for these four tests. The water in the reservoir became covered with a *skin*, presumably of iron hydroxide (not analysed), a short time after the start of the tests.

The analytical results in Table I indicate that the various heavymetal concentrations were reduced to varying extents. Maximum reductions found were as follows: Fe - 99.9%; Mn - 52.2%; Cu - 53.0%; Pb - 93.3%; and Zn - 92.8%. The calcium-ion concentration in the solutions increased as a result of the following reactions:

	$Fe^{++} \rightarrow Fe^{+++} + e$ (oxidation)	(1)
	$Fe^{+++} + 3H_20 \rightarrow Fe(0H)_3 \text{ pptd} + 3H^+ \text{ (hydrolysis)}$	 (2)
•	$3H^+ + 3CaCO_3 \rightarrow 3Ca^{++} + .3HCO_3^-$ (neutralization)	(3)

The sulfate concentrations were reduced by precipitation of some $CaSO_4$ as a result of supersaturation caused by the increasing Ca^{++} content:

 $Ca^{++} + SO_4^{-} \Rightarrow CaSO_4 pptd$

The increases in C1⁻ content are caused by leakage of KC1 from the reference electrode during the tests; the analysis for the longest test, number II, shows the highest C1⁻ content.

(4)

Synthetic acidic waters: The results of the first three tests with synthetic acidic water (Figs. 2, 3 and 4) show a common behaviour; an initial rapid rise in pH to about 5.5 is followed by a slow rise to about 6.7, after which the pH increases somewhat more rapidly to values between 7.5 and 8.0. The Eh, after an initial drop ranging from 90 to 110 millivolts, and a rebound of between 70 and 80 millivolts, dropped relatively steadily in less than 1 hour to values of +110, +105 and +170 millivolts (runs 1, 2 and 3, respectively), followed by a further gradual decrease to values of -20, -40 and +40 millivolts, respectively. In these same three tests, a rapid increase in Eh started after 70, 40 and 15 hours, respectively, coinciding with the more rapid rise in pH. The water in the reservoir became again *crusted over* with a persistent *skin* presumably of iron hydroxide, which prevented aeration.

The smaller drops in Eh, and the more rapid reaction during run #3 were presumably caused by the entry of air bubbles into the circulation system, through the stopper at the top of the limestone-filled tube. This was confirmed by the results of the next test, in which air was bubbled at a high rate through a porous ceramic cup, into the water reservoir (Figs. 5a and 5b). The initial pH rise (to 5.8 in this case) still occurred, followed by a slow further rise to about 6.5, and a more rapid rise to 8.0. The initial drop in Eh, only 55 millivolts, was smaller than before, and the ensuing rise of about 70 millivolts raised the Eh slightly above its original value. Subsequently the Eh decreased fairly rapidly to about +540 millivolts, decreasing further at a much slower rate to a minimum of +474 millivolts; this was followed by an increasingly rapid rise to +550 millivolts and a renewed decrease to the final value, +415 millivolts. The last rapid increase in redox potential again coincided with the accelerated rise in pH. All consecutive decreases and increases in the redox potential found in tests 1, 2 and 3 are thus represented in the results of test 4; however, the minimum Eh value in test 4 was at least 435 millivolts higher than that

in the other tests. The reversal in the Eh trend, and the accelerated rise in pH, occurred within less than three hours, rather than the 15 to 70 hours reported for tests 1 - 3, presumably as a result of the intensive aeration.

In addition it should be mentioned, that no *skin* was formed on the water in the reservoir during test 4; the resulting precipitate was more powdery than in the earlier tests, and the water needed no filtering.

The influence of aeration on the neutralization process was described earlier, in terms of pH only, by Mihok *et al* (1968). The aeration rapidly removes dissolved carbon dioxide from the solution, making it possible to achieve a higher pH within a shorter time. A comparison of the behaviour of the redox potential in tests 1 to 4 leads to the additional conclusion that the aeration also improves the rate of oxidation from Fe⁺⁺ to Fe⁺⁺⁺. Without aeration, the redox potential stays at a low value for a long time, simultaneously preventing the neutralization from proceeding, while acidity is slowly but continuously being formed.

The results of tests 5 and 6 (Figs. 6 and 7) show the same general characteristics of consecutive rapid, slow and more rapid increase in pH, and three periods of decreasing Eh alternating with two periods of increasing Eh. The pH reached final values of 7.93 and 7.96, respectively; the Eh values at the end of the tests were +454 and +472 millivolts, respectively. The last increase in Eh and the final rapid rise in pH in these tests started after less than an hour. The reaction was most rapid in test 6. The Eh in this test went through a minimum value of +320, as compared to a minimum of +435 millivolts in test 5.

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During the circulation tests, 1 through 4, the water being treated was in contact with the limestone for approximately 5 per cent of the time only. It could thus be expected, that the reactions with $CaCO_3$ powder in tests 5 and 6 would be completed about 20 times as fast as in test 4. In fact, the final pH of 7.9 was reached only about 6 times as fast as in test 4. This may indicate that the contact between water and limestone in the column during the earlier test was more efficient than the contact between water and $CaCO_3$ powder during the latter tests. On the other hand, if the oxidation from Fe⁺⁺ to Fe⁺⁺⁺ is the rate-determining step (Singer and Stumm, 1970), then the additional time spent by the water in the aerated reservoir during the circulation tests may account for the smaller-than-expected difference in reaction times.

The water produced by the last two tests needed double filtering; in the other tests, at least the first 1/3 of the water was clear when pumped into the sample bottles. The water from test 4 needed no filtering at all.

The analyses of the water produced by the tests on synthetic acidic water (Table II) indicate the following maximum reductions in heavy-metal concentrations: Fe - 99.8%; Al - 96.6%; Mn - 35.7%; Cu - 99.8%; Pb - > 99.9%; Zn = 97.1%. The calcium concentrations increased again during these tests as a result of dissolution of limestone (or CaCO₃ powder).

CONCLUSIONS

A comparison of the results obtained for the synthetic acidic water (Table II) and the natural acidic water (Table I) shows that, for some of the ions, a minimum concentration is approached which seems to be independent of the original concentration in the solution. The respective minimum values in ppm, for the natural and synthetic water, are: Fe 0.05 and 0.6; A1 < 0.3; Mn 0.22 and 4.5; Cu 0.008 and 0.006; Pb < 0.01 and 0.002; Zn 3.7 and 5.0.

Neutralization of acidic water with a high heavy-metal content by circulation through crushed limestone, appears to result in removal of most of the dissolved Fe, Al, Cu and Pb, and much of the Zn; Mn is only partially removed. The process therefore holds some promise for the treatment of acidic heavy-metal bearing drainage from sulfide-ore mines, dumps and tailing ponds. It is not known whether the presence of partially reduced sulfur species will affect the effectiveness of the process in any way.

The sludge resulting from the neutralization process has better settling characteristics (smaller sludge volume) if limestone is used than if lime is used (Mihok *et al.*, 1968); in addition, the raw material is often readily available where needed. The process could be favoured over other heavy-metal extraction processes by virtue of the fact that only natural materials are involved, as opposed to synthetic organic extractants. The problem of sludge disposal is similar to that experienced when distillation (flash evaporation) or reverse osmosis are employed to treat the water. Thus, further investigation into possible wider application of the limestone neutralization process may be worthwhile.

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Singer, P.C. and W. Stumm. 1970. Acidic mine drainage - The rate-determining step. Science, 167: 1121-23.

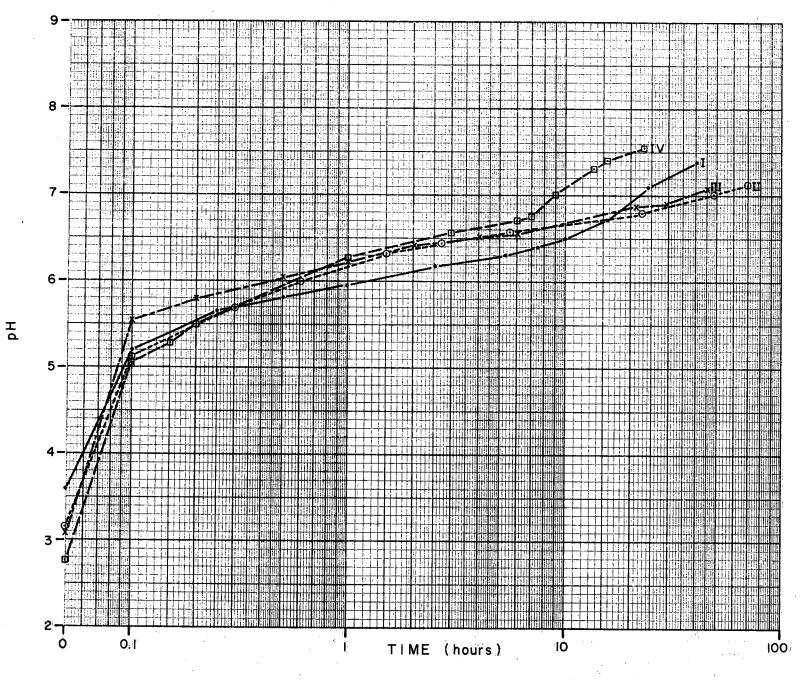


Figure 1. pH vs time for acidic spring water (tests I to IV).

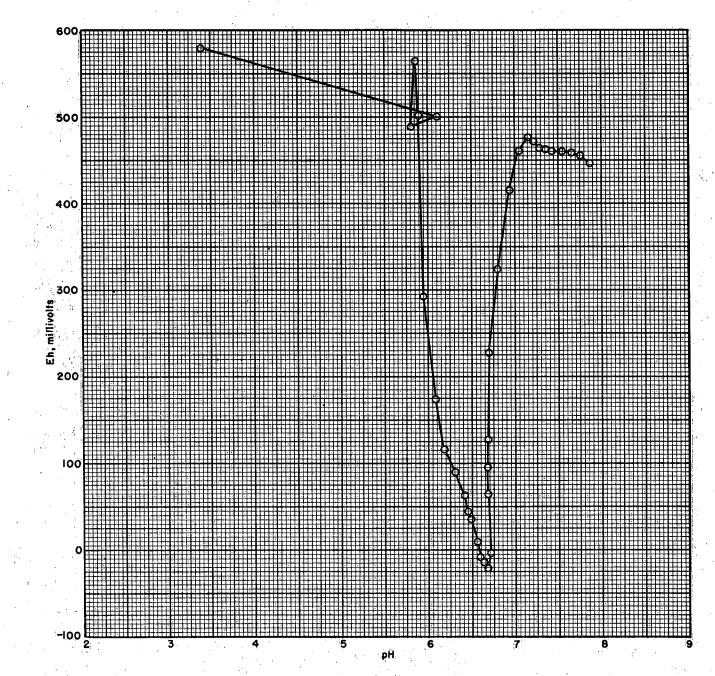


Figure 2a. pH vs Eh for synthetic acidic water (test 1).

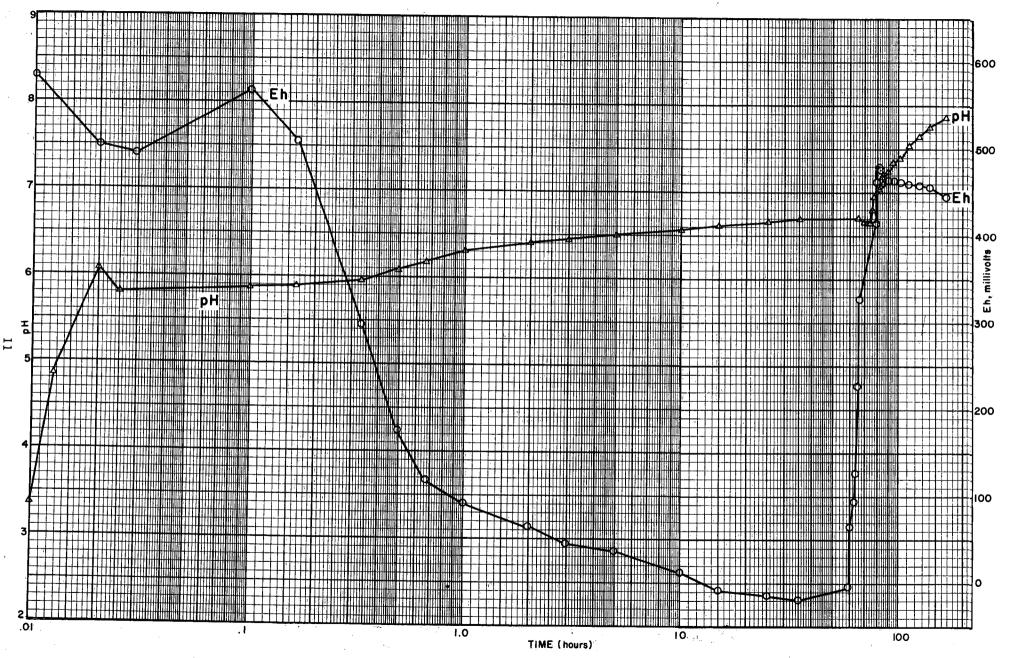


Figure 2b. pH and Eh vs time for synthetic acidic water (test 1).

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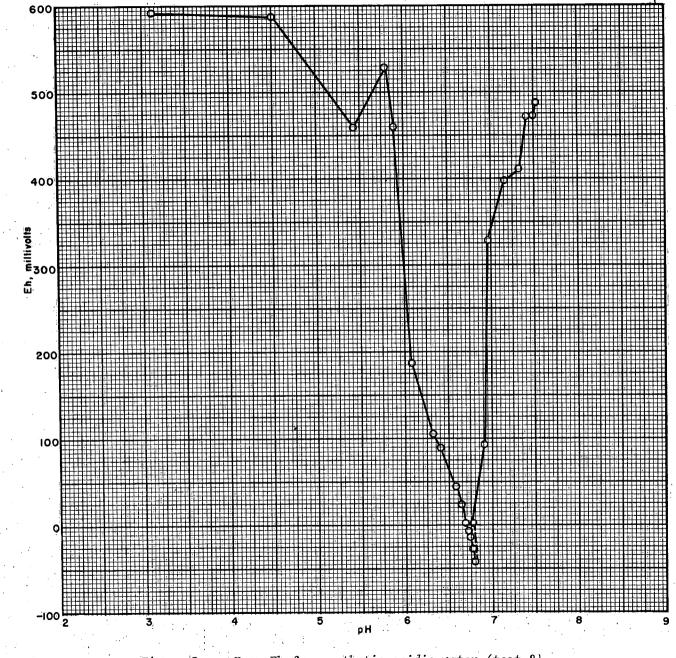
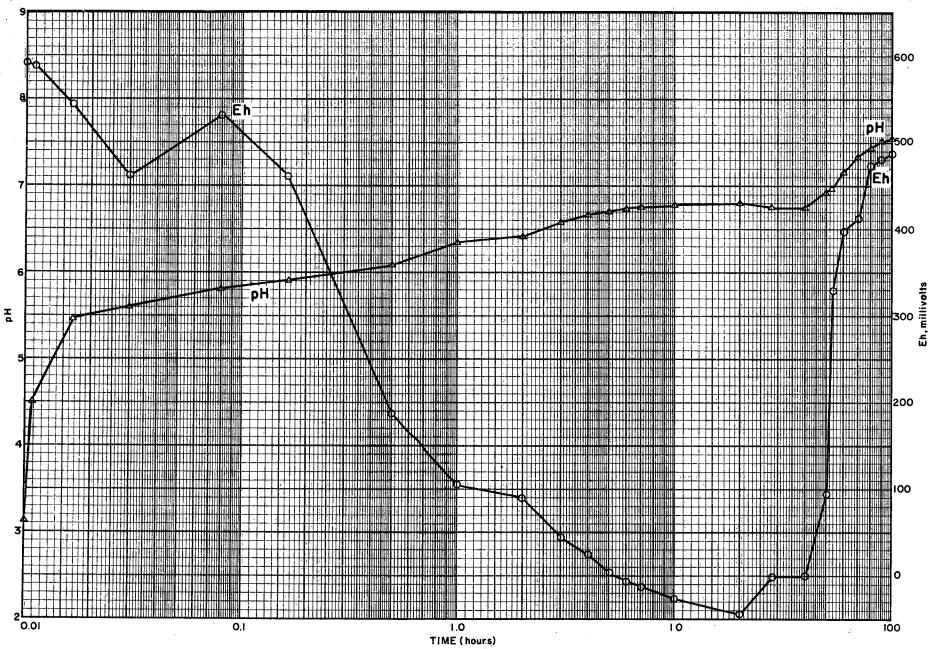


Figure 3a. pH vs Eh for synthetic acidic water (test 2).

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Figure 3b. pH and Eh vs time for synthetic acidic water (test 2).

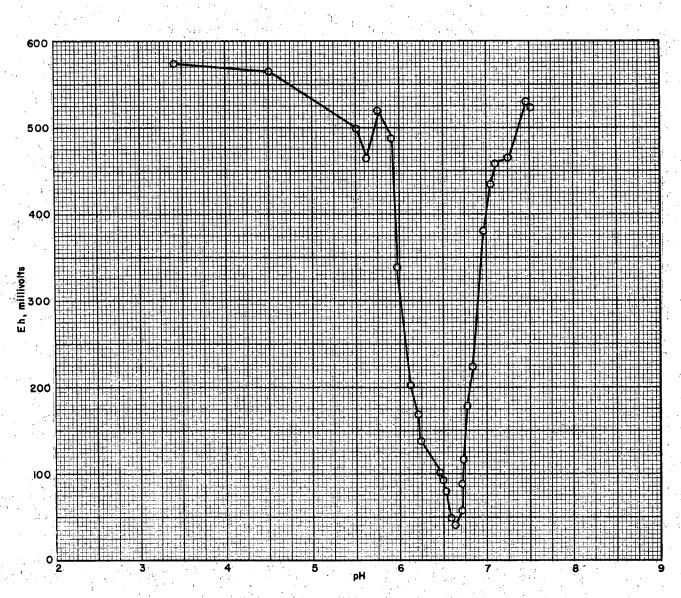


Figure 4a. pH vs Eh for synthetic acidic water (test 3).

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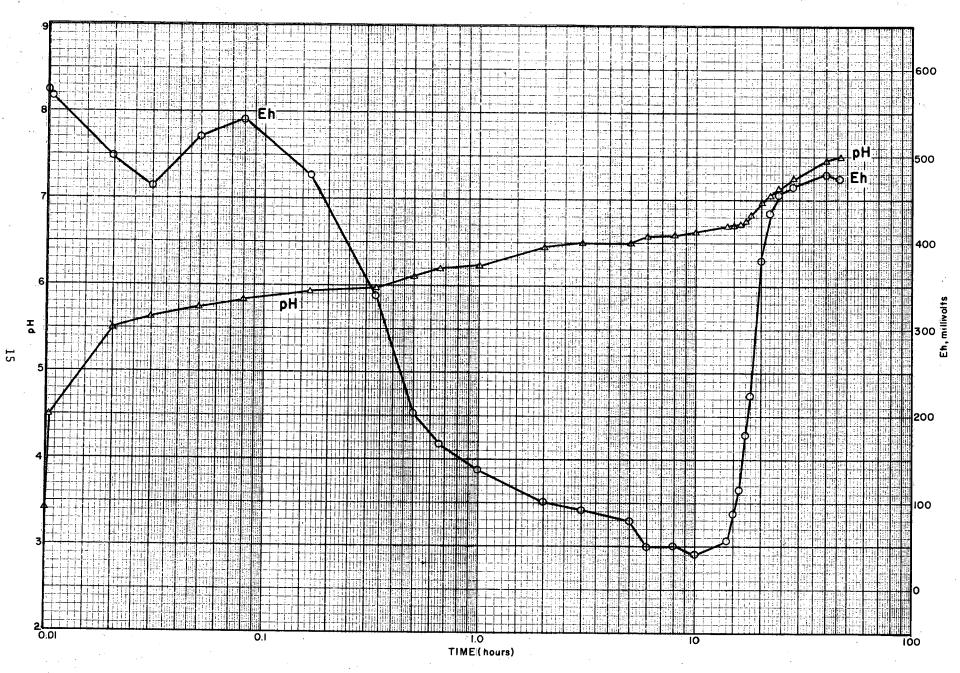


Figure 4b. pH and Eh vs time for synthetic acidic water (test 3).

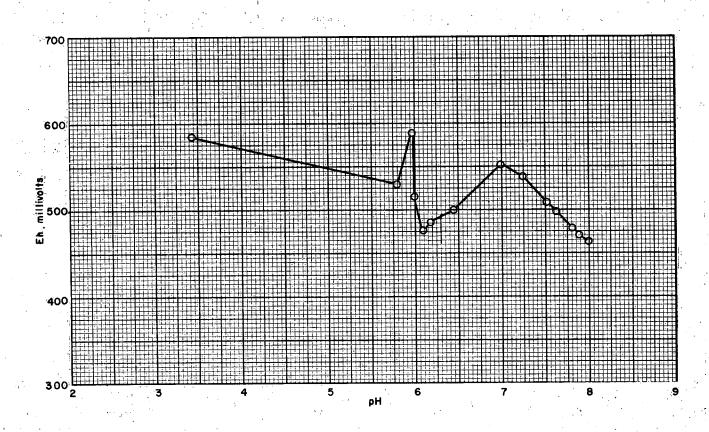


Figure 5a. pH vs Eh for synthetic acidic water (test 4).

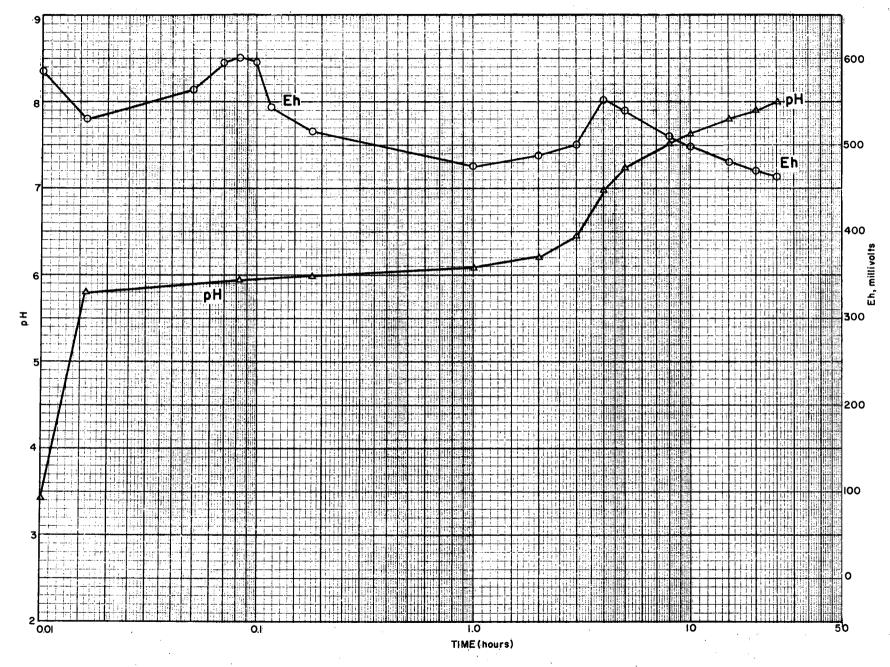


Figure 5b. pH and Eh vs time for synthetic acidic water (test 4).

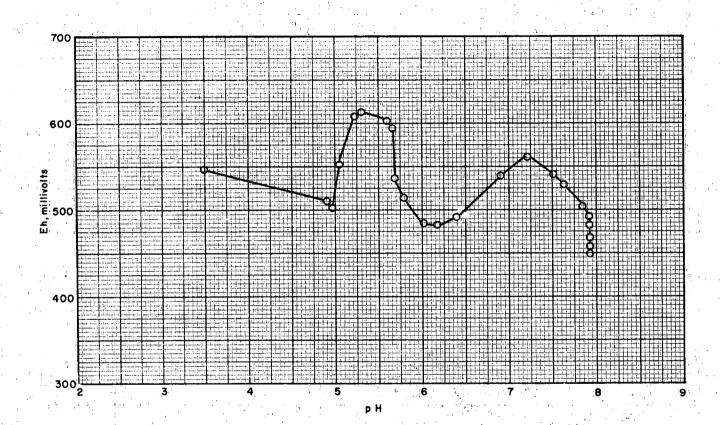


Figure 6a. pH vs Eh for synthetic acidic water (test 5).

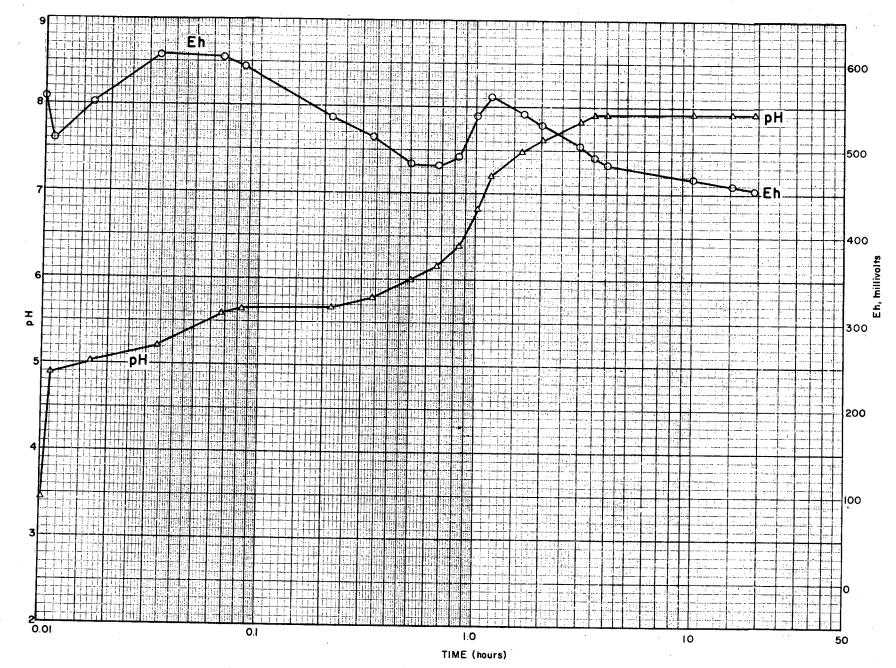


Figure 6b. pH and Eh vs time for synthetic acidic water (test 5).

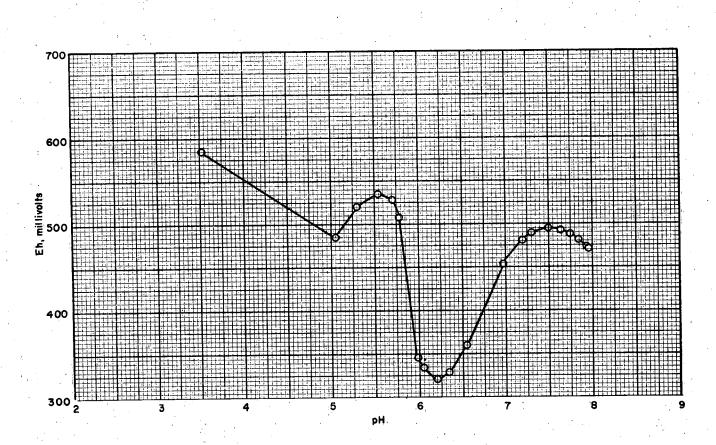


Figure 7a. pH vs Eh for synthetic acidic water (test 6).

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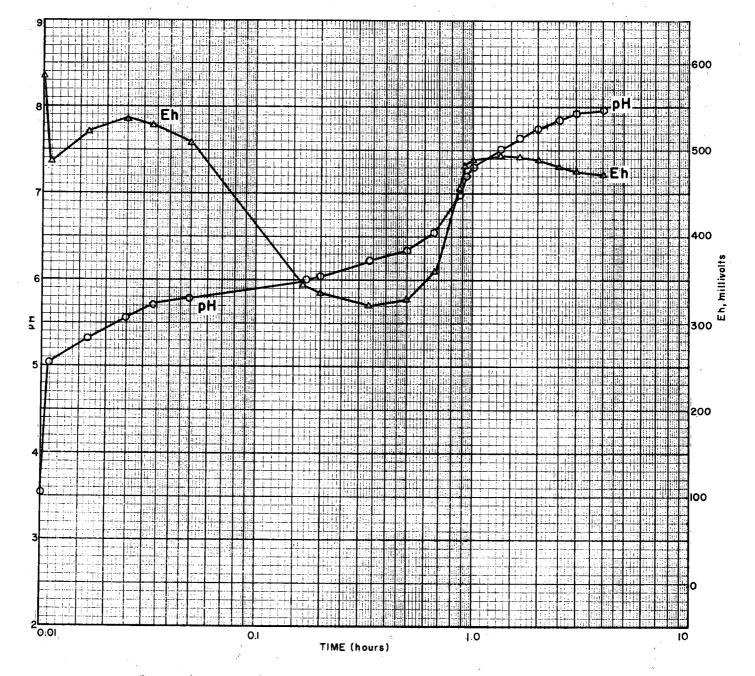
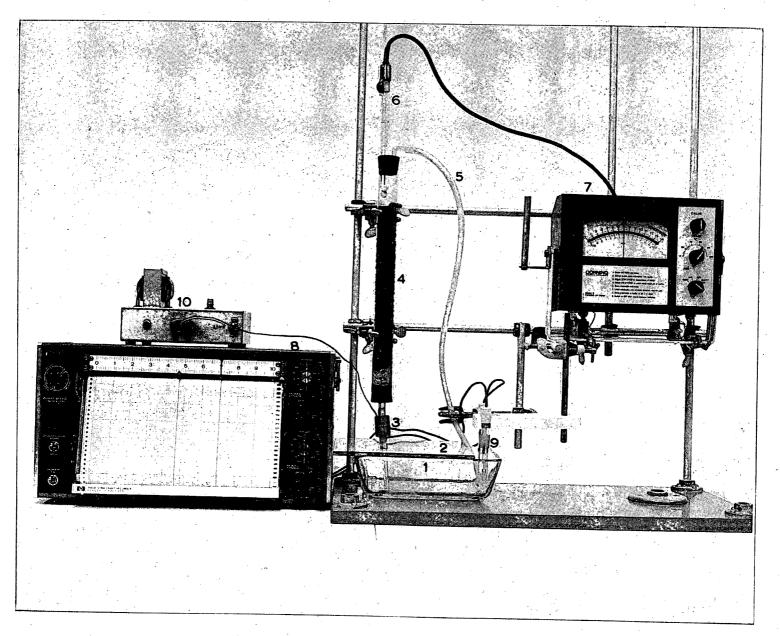


Figure 7b. pH and Eh vs time for synthetic acidic water (test 6).



Equipment used in limestone neutralization test.

Current Technical Bulletins

No. 24 Application of Regression Analysis in Hydrology. N. Tywoniuk and K. Wiebe, 1970.

A description of the applications (and limitations) of regression analysis and a discussion of the distinction between regression – and correlation analysis.

No. 25 Stream Gauging Techniques for Remote Areas Using Portable Equipment. M. Church and R. Kellerhals, 1970.

A review of streamflow measuring techniques applicable to rivers with peak flows up to 10,000 cfs.

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