

# Treatability Trials to remove Zinc from Abbey Consols Mine Water, Wales, UK

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## Abstract

Abandoned metal mines are a principal cause of European Union Water Framework Directive (WFD) standards failures in Wales, with 1,300 mines affecting over 700 km of rivers. Abbey Consols lead-zinc mine discharges  $\approx 3$  kg day<sup>-1</sup> of zinc to the River Teifi, causing WFD failures for at least 14 km. This paper presents results of laboratory and field trials to identify an effective method to remove zinc from Abbey Consols mine water. Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) dosing to raise pH and facilitate precipitation is shown to offer an efficient and cost-effective treatment solution, achieving >90% reduction in dissolved zinc concentrations.

**Keywords:** Metal Mine Remediation, Water Framework Directive, Field Trial, Sodium Carbonate Dosing

## Introduction

The abandoned Abbey Consols mine, near Strata Florida Abbey, Mid Wales, has been identified as the primary source of zinc to the River Teifi Special Area of Conservation (SRK 1997; ExCAL 1999; Environment Agency Wales 2012). Contaminated groundwater emerges from a pipe in the northeast of the site, approximately 30 m downgradient of the buried deep adit. This flows in a channel around the former dressing floors, receiving seepages and run-off from waste tips, before discharging to the River Teifi. An extensive ground investigation was undertaken in

2019 to improve the conceptual site model, and to locate the buried adit and confirm the origin of the groundwater pipe discharge. The adit was not located but a pronounced groundwater flow in its vicinity was. A standpipe was installed, enabling the adit water to be sampled (Table 1) and collected in bulk for treatability trials.

An hydrochemical assessment (WSP 2019) found that the groundwater pipe discharge contains a combination of adit water and cleaner groundwater. Some of the adit discharge was also found to follow a groundwater pathway into the waste tips.

*Table 1 Selected chemistry of Abbey Consols mine water sampled from adit standpipe.*

Total µgL <sup>-1</sup>	Min	Mean	Max
Alkalinity (as CaCO <sub>3</sub> )	23,700	28,667	31,500
Sulfate	28,400	34,800	40,600
pH	6.62	6.92	7.11
Zinc	14,700	16,267	17,700
Lead	594	3,688	6,790
Cadmium	36	40	45
Iron	2,210	20,293	50,700

As the adit discharge flows into and interacts with water in the waste tips, and the emerging seepages and run-off from the waste tips flow into the groundwater pipe channel, it is not possible to accurately apportion the metal load from the site between these two main sources. To achieve the WFD zinc (dissolved bioavailable) standard of  $13.4 \mu\text{gL}^{-1}$  in the River Teifi, zinc load from the site as a whole would need to be reduced by at least 70%. The remediation works being designed by WSP aim to achieve this by separation of the adit water from the waste tips and transfer to a mine water treatment system. The waste tips will be hydraulically isolated through capping and drainage. This paper presents results from laboratory and field trials to develop the mine water treatment solution.

### Laboratory trials: iron dosing with limestone pre-treatment

A treatment options appraisal (WSP 2018) concluded that removal of zinc from the mine water via coprecipitation and sorption during iron precipitation may be a suitable solution. In the absence of elevated dissolved iron concentrations in the mine water, chemical dosing would be required. To assess the feasibility of iron dosing, establish optimum removal rates and to refine the likely concentrations required, laboratory trials were undertaken in May 2019. A limestone pre-treatment step was included due to concerns of lowering pH associated with iron dosing. The aim was to identify the optimum contact time between mine water and limestone gravel that resulted in the largest increase in pH and alkalinity. Limestone gravel of 10-14 mm from B&Q DIY store was washed with deionised water to remove fines that could artificially skew

the pH. Four 12 L buckets were filled with the gravel and 680 mL of mine water was added to each. The buckets were placed on an orbital shaker for 2, 5, 15 or 45 min and water was carefully decanted for analysis at each interval. The 45 min exposure resulted in an increase in pH from 6.85 to 8.33 and in alkalinity from  $23 \text{mgL}^{-1}$  to  $374 \text{mgL}^{-1}$  (Table 2). There was also a concurrent reduction in dissolved zinc concentrations of up to 94%. Hydrochemical modelling indicated the formation of a zinc carbonate to be the likely precipitation process.

Following the limestone pre-treatment tests the mine water was decanted from the buckets into beakers for the iron dosing tests. The aim was to establish the effect on zinc removal of dosing with different concentrations of iron (II) (ferrous) sulfate and iron (III) (ferric) sulfate hydrate. At the time of testing the zinc removal results of the limestone pre-treatment tests were unknown, therefore the dosing tests generally produced unrepresentative results as much of the zinc had already precipitated. It is not known how much the test results were affected by iron precipitation; enabling removal of zinc but potentially also enabling zinc carbonates to re-dissolve with the lowering of pH. These first laboratory trials offered a new opportunity for simplifying the mine water treatment solution relative to the original iron dosing and precipitation approach. It was decided further testing should focus on removal of zinc as a zinc carbonate.

### Laboratory trials: carbonate sources and multiple contact cycles

A second set of laboratory trials were undertaken in August 2019 to test a range of limestone sources, repeat contact of mine

Table 2 Results of different exposure times of mine water to B&Q limestone gravel.

Contact time	Zinc diss. ( $\mu\text{gL}^{-1}$ )	Zinc diss. (% removal)	pH	Alkalinity, Tot. as $\text{CaCO}_3$ ( $\text{mgL}^{-1}$ )
Raw mine water	15,900	-	6.85	22.8
2 min	9,590	40	6.94	65.0
5 min	6,530	59	7.36	262
15 min	2,940	82	7.77	120
45 min	922	94	8.33	374

water with the limestone and dosing with carbonate-containing reagents as a substitute for limestone. Chalk (20 mm grain size) and two different types of limestone gravel with grain sizes of 16-32 mm (Abergele) and 20 mm (Penderyn) were tested. The chalk and limestone gravels were pre-washed with tap water in a sieve for 5 min, then rinsed with deionised water to remove fines that could misrepresent the long-term behaviour of the limestone and lead to only temporary effects on pH and alkalinity or produce suspended solids which did not arise from the reaction with mine water. A total volume of 0.0048 m<sup>3</sup> of the chalk and two limestone gravels were each placed in 12 L buckets with a 10 mm hole drilled in the bottom and a bung in place. Mine water (750 mL) was added and left undisturbed for either 15 min, 45 min or 2 h. After each exposure period the water was rapidly drained from the bucket into a glass beaker to ensure all suspended solids, as far as possible, were decanted. To measure settlement rates samples of the decanted solution were gathered 1 cm from the surface 15 min, 45 min and 2 h following decanting. Once the contact and settlement time had lapsed the liquid was drained through a glass microfiber filter and dried overnight to determine the quantity of precipitate. Samples of the filtered water were collected for laboratory analysis (Table 3).

The 2 h exposure to chalk resulted in the largest reduction in zinc concentrations relative to the Abergele and Penderyn gravels, as well as the largest quantity of precipitate. Penderyn gravel resulted in equal alkalinity

to chalk over the 2 h exposure period, but a lower pH and more limited zinc precipitation. The B&Q gravel used in the May 2019 laboratory tests resulted in greater alkalinity and zinc removal than any of the three gravel sources used here. Overall, high zinc removal rates (>90%) seem to be achievable within a pH range of 8-8.5, but the mass of precipitate formed may be a concern for a full-size system due to disposal costs.

Chalk gravel was selected to test whether zinc removal efficacy is maintained following multiple cycles of contact between mine water and gravel. Fresh chalk was washed with deionised water to remove fines and was placed into a 12 L bucket with a 10 mm hole drilled in the bottom and a bung in place. Mine water (750 mL) was added and left undisturbed for 45 min, after which the water was drained. The process was repeated a total of ten times with fresh mine water on each occasion. Following the first, third, fifth, seventh and tenth exposures precipitate was measured using glass microfiber filters and the filtered liquid was sent for laboratory analysis (Table 4). The repeat exposure of the chalk to fresh mine water resulted in a steady decline in zinc removal rate from 84% to 61%. pH declined from 8.08 to 7.77 and the quantity of precipitate declined from 0.500 g to 0.295 g. This suggests that the efficacy of limestone gravel treatment may diminish over time, however, the test would need to be carried out for longer to establish if the removal rates stabilise or continue to reduce. The final laboratory tests investigated the efficacy of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>)

*Table 3 Selected results following 45 min and 2 h exposure of mine water to different gravel sources, followed by a 2 h settling time and glass microfiber filtration.*

Treatment	Zinc diss. (µgL <sup>-1</sup> )	Zinc diss. (% removal)	pH	Alkalinity, Tot. as CaCO <sub>3</sub> (mgL <sup>-1</sup> )	Weight of precipitate (g)
Raw mine water	16,100	-	6.92	32.9	-
Chalk 45 min	5,520	66	7.86	42.5	0.7448
Chalk 2 h	1,080	93	8.10	50.0	0.7366
Abergele 45 min	9,240	43	7.58	35.0	0.1397
Abergele 2 h	4,280	73	7.77	42.4	0.1052
Penderyn 45 min	9,670	40	7.68	46.5	0.1019
Penderyn 2 h	3,810	76	7.85	50.0	0.1238

*Table 4 Selected results following repeat contact cycles between chalk gravel and mine water.*

Treatment	Zinc diss. ( $\mu\text{gL}^{-1}$ )	Zinc diss. (% removal)	pH	Alkalinity, Tot. as $\text{CaCO}_3$ ( $\text{mgL}^{-1}$ )	Weight of precipitate (g)
Raw mine water	16,100	-	6.92	32.9	-
Cycle 1	2,510	84	8.08	43.5	0.4997
Cycle 3	3,620	78	7.93	40.1	0.3872
Cycle 5	4,450	72	7.97	50.0	0.3696
Cycle 7	4,860	70	7.88	45.0	0.3228
Cycle 10	6,350	61	7.77	43.1	0.2953

*Table 5 Selected results following dosing of mine water with  $\text{Na}_2\text{CO}_3$  and 2 h standing time.*

Treatment zinc: $\text{Na}_2\text{CO}_3$ ratio	Zinc diss. ( $\mu\text{gL}^{-1}$ )	Zinc diss. (% removal)	pH	Alkalinity, Tot. as $\text{CaCO}_3$ ( $\text{mgL}^{-1}$ )	Weight of precipitate (g)
Raw mine water	16,100	-	6.92	22.8	-
$\text{Na}_2\text{CO}_3$ 1:1	6,920	57	7.75	38.5	0.0100
$\text{Na}_2\text{CO}_3$ 1:2	960	94	8.43	55.0	0.0202
$\text{Na}_2\text{CO}_3$ 1:2.5	123	99	9.27	63.8	0.0225

dosing at different concentrations on the precipitation of zinc and the associated affect on pH. Mine water (1 L) was placed in beakers on a magnetic stirrer and a stock solution of 2.586 g  $\text{Na}_2\text{CO}_3$  in 1 L of deionised water was made. The  $\text{Na}_2\text{CO}_3$  solution was then added to the beakers of mine water at zinc: $\text{Na}_2\text{CO}_3$  ratios of 1:1 (10 mL), 1:2 (20 mL) and 1:2.5 (25 mL). Following reagent addition samples were taken for laboratory analysis. The turbidity of the water and the rate at which settlement of suspended solids occurred was then recorded by visual observations and a photographic record over 2 h. Once the 2 h had lapsed samples were filtered using glass microfiber filters to quantify the amount of precipitate formed, and the liquid was subject to laboratory analysis (Table 5). Standing time during the experiment appeared to have minor beneficial influence on the results and only those following the 2 h period are presented.

Sodium carbonate dosing at a ratio of 1:1 and 2 h standing time resulted in an increase in pH to 7.75 and a reduction in dissolved zinc of 57%. This improved with increased  $\text{Na}_2\text{CO}_3$  dosing rates to a maximum of 99% at a 1:2.5 ratio, although the resulting pH of 9.27 was greater than the target maximum

of pH 9. No visible turbidity was apparent in the water following  $\text{Na}_2\text{CO}_3$  dosing and the precipitate mass was very low.

The laboratory trials indicated that raising the mine water pH to 8-8.5 via provision of a soluble carbonate source and subsequent precipitation of zinc as a carbonate could be an effective treatment solution. The use of limestone gravel may be a higher risk option due to decreased efficacy over time and the amount of precipitate generated. Dosing of mine water with  $\text{Na}_2\text{CO}_3$  may offer a highly efficient, relatively cheap and non-hazardous treatment solution. A non-hazardous reagent is particularly important for a remote and environmentally sensitive setting as Abbey Consols. The treated water has a reduced zinc concentration and its water type is similar to local surface water, lessening any potential impact from the discharge. Treatment volumes in the laboratory were too low to measure settlement behaviour of the zinc carbonate and there was a risk that precipitate could remain suspended in the treatment effluent. It was decided these factors should be assessed through short-term field trials before finalising the design of a large-scale demonstration system.

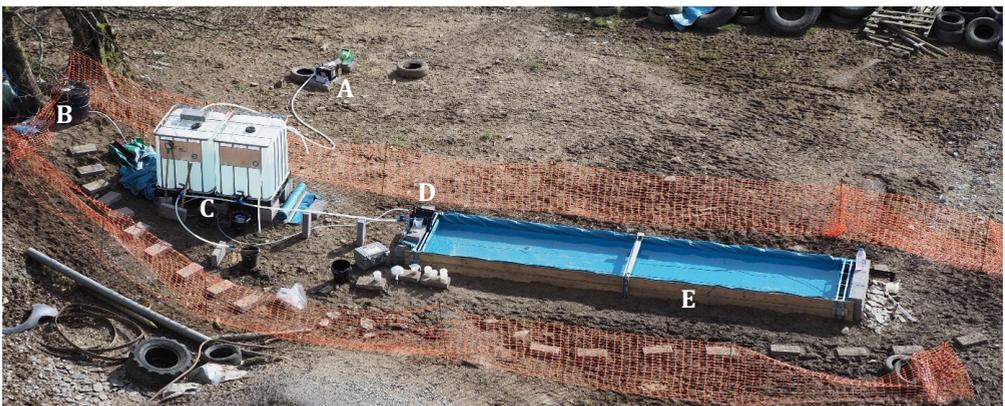
### Field trials: sodium carbonate dosing

A small-scale field trial was designed to test  $\text{Na}_2\text{CO}_3$  dosing with a continuous higher volume flow of mine water and investigate the settlement rate and characteristics of the precipitate formed. The aim was to generate 1 kg of precipitate, requiring an estimated  $40 \text{ m}^3$  of mine water to be processed. The dosing requirements targeted a pH that would provide a maximum zinc removal rate but remained  $\text{pH} < 9$  to allow discharge to the environment. The laboratory trials suggested that a dosing ratio of 1:2 (zinc: $\text{Na}_2\text{CO}_3$ ) would provide a pH of  $\approx 8.4$  and remove  $\approx 94\%$  of zinc. The trial commenced on 16<sup>th</sup> March 2020 but had to be suspended on 24<sup>th</sup> March due to the implementation of coronavirus restrictions. The trial relied on a simple, temporary facility (Figure 1). Mine water was pumped from the adit standpipe to two intermediate bulk containers (IBCs) to provide the mine water feed. A dosing tank was filled with a  $2.6 \text{ gL}^{-1}$  solution of  $\text{Na}_2\text{CO}_3$  made on site by weighing out powdered  $\text{Na}_2\text{CO}_3$  and mixing with deionised water. The dosing tank and the mine water IBCs were connected to a mixing tank and the flows from each controlled by taps. The mixing tank released the dosed mine water via several outfalls to promote laminar flow into the settling pond (6.6 m  $\times$  1.3 m). Treated mine water flowed through the settling pond before draining via an outflow at the far end. The typical volume held in the settling pond during operation was  $2.36 \text{ m}^3$

and the typical inflow rate was  $0.18 \text{ L s}^{-1}$ , providing a retention time just under 4 hours. The dose of the  $\text{Na}_2\text{CO}_3$  solution was varied with the tap to maintain the target pH of 8.4 in the settling pond.

Total operation time was 31 h 17 min, treating 19,813 L of mine water with 427 L of  $\text{Na}_2\text{CO}_3$  dosing solution. The dose equates to between 80 and  $100 \text{ L day}^{-1}$ , and the ratio of zinc: $\text{Na}_2\text{CO}_3$  was on average 1:2.2, but at times reached as high as 1:3.1. Flow measurements were taken from the inflow, dosing tap and outflow using a stopwatch and measuring jug. Water samples were taken from the mine water inflow and the treatment outflow twice per day (Table 6). The zinc removal rate per sample set (one inflow and one outflow taken at the same time) are also presented.

The average mine water inflow pH measured in the field was 7.8, slightly higher than laboratory analyses and also previous field measurements of pH from the adit standpipe (Table 1). The average pH achieved in the settling pond (8.3) was slightly lower than targeted (8.4). This is attributed to the sensitivity of dosing control with the tap installation, including optimisation required following dilution by rainfall. At full-scale the dose control will be finer, managed via an automated system triggered by the settling pond pH. Dissolved zinc removal ranged from 58-91% and total zinc removal ranged from 27-61%, the highest removal rates both coinciding with the highest pH of 9.69. The



**Figure 1** Arrangement of field trial at Abbey Consols. Adit standpipe (A), dosing solution tank (B), mine water IBCs (C), mixing tank (D) and settling pond (E).

*Table 6 Zinc removal rates between inflow and outflow for individual samples.*

Sample date/time	Mine water flow (Ls <sup>-1</sup> )	Zinc:Na <sub>2</sub> CO <sub>3</sub> ratio	Mine water inflow field pH	Settling pond field pH	Zinc diss. (% removal)	Zinc tot. (% removal)
17/03/2020 12:00	0.167	1:3.1	7.77	8.10	62	32
17/03/2020 16:00	0.167	1:3.1	7.88	8.10	63	27
18/03/2020 11:00	0.163	1:2.1	7.57	9.69	91	61
18/03/2020 15:55	0.163	1:2.1	7.90	8.12	79	35
19/03/2020 11:00	0.181	1:2.2	7.80	8.60	83	42
19/03/2020 14:50	0.181	1:2.2	7.90	8.10	58	31
19/03/2020 16:20*	-	-	-	8.30	68	20
20/03/2020 10:00*	-	-	-	7.90	69	65
20/03/2020 11:20	0.165	1:1.4	7.83	8.50	75	49
23/03/2020 16:13	0.206	1:2.1	7.77	8.53	86	36
24/03/2020 10:00*	-	-	-	8.16	81	82
24/03/2020 10:00	0.190	1:1.8	7.90	8.46	87	54

\*settling pond sample.

difference between dissolved and total zinc removal efficiency indicates the settling pond retention time was too short, with precipitate being lost in the outflow. It is also suspected that wind turbulence may have affected how well the precipitate settled.

Three settling pond samples were taken to investigate if standing time affected zinc removal or precipitation overnight (Table 6). On 19<sup>th</sup> March the settling pond sample showed a much higher dissolved zinc removal rate than total zinc as it was taken following a day of treatment (i.e. no additional settling time). The settling pond samples taken on 20<sup>th</sup> and 24<sup>th</sup> March were at the beginning of the day before the treatment system was restarted, indicating the potential removal rate following over 12 h of additional settling time. Although the dissolved zinc removal rates were similar to the operating conditions, the total zinc removal rates were much higher, essentially matching those of dissolved metals, and for the 24<sup>th</sup> March reached over 80%. The change in removal rates following a longer retention time within the settling pond indicates that the precipitate settling rate is longer than the 3-4 h of the trial. A white precipitate began to form in the settling pond within 1 m of the inflow by the second day of operation and a sample was collected on 23<sup>rd</sup> March in anticipation of the trial being suspended the following day. The

precipitate was allowed to settle in measuring jugs before being filtered with a sieve and paper towel. It was then sealed in a container for transport to the laboratory.

The wet weight of the sample measured on site was between 800-900 g and moisture content of the precipitate was 95%. The zinc concentration was 46%, however, the total inorganic carbon was only 1.2%, much lower than expected if a pure zinc carbonate was forming. The ratios of zinc to carbon suggest it's more likely to be hydrozincite (Zn<sub>5</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub>), although potentially with some additional metal precipitate. Hydrozincite is less dense than smithsonite and potentially more easily resuspended, which will therefore benefit from optimisation of the settling time.

## Conclusion

Treatability trials identified that dosing with Na<sub>2</sub>CO<sub>3</sub> as a carbonate source and raising pH to ≈8.5 can successfully remove >80% of dissolved zinc from Abbey Consols mine water in the field. Over 90% zinc removal was also shown to be achievable, but with a corresponding pH considered too high for discharge to the environment. During the field trial total zinc removal was lower during operation than following overnight standing time in the settling pond, indicating a larger surface area of the pond and protection from

turbulence caused by wind are required to settle the precipitate more efficiently for the flow rate treated. The large-scale demonstrator system will target pH 8.5-9 and is being designed to allow comprehensive testing of precipitation and settlement behaviour and to explore the precipitation of hydrozincite versus smithsonite. Mechanisms to reduce the water content of the precipitate will also need to be considered in the design to reduce disposal costs. Although the flow rate from the buried adit is currently unconfirmed, it is considered the mine water treatment, in combination with the mine waste capping works, can achieve the >70% reduction in zinc load required to achieve WFD targets.

### **Acknowledgements**

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