

REPORT

THE EFFECTIVENESS OF CDE 2 TO EXTRACT METALS FROM GEOLOGICAL AND ENVIRONMENTAL MATERIALS

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SCOPE OF STUDY

GENERAL: This Project has been designed to test the capabilities of the CDE 2 solution, as supplied by AMAI, to extract metals from a variety of earth materials (see section on descriptions of samples) ranging from powdered rock samples of known chemistry, to mine ore concentrates and tailings, to anthropogenically contaminated sediments collected adjacent to heavy industrial activity. The tests have been designed to use, with as few modifications as possible, the standard procedures in use in the CAEAL-accredited GLIER analytical laboratories.

METHODOLOGIES:

A. Sample Extractions

1. “Cold” extractions - One gram samples (in triplicate) were weighed into 50ml polycarbonate tubes and reacted with 5 grams of CDE 2 solution in a tube shaker for fixed times of 10 minutes, 30 minutes and 60 minutes at room temperature (22°C). After shaking, the sample residue was separated from the reacted CDE 2 solution by centrifugation followed by filtration (#415 filter paper). The filtered CDE 2 solution was diluted to 250 grams with 1% nitric acid (ACS grade) in 250ml LDPE bottles and stored for analysis. The solid residue, after rinsing and centrifuging 3 times with laboratory water (MilliQ), was saved for possible subsequent experiments.
2. Variable temperature extractions - One gram samples of sulphide ore concentrate WMS-1 (in triplicate) were weighed into 50ml polycarbonate tubes and reacted with 5 grams of CDE 2 solution at temperatures of 30°C, 60°C and 90°C. The sample residue was separated from the reacted CDE 2 solution by centrifugation followed by filtration (#415 filter paper). The filtered CDE 2 solution was diluted to 250 grams with 1% nitric acid (ACS grade) in 250ml LDPE bottles and stored for analysis.
3. Solid residue analysis - The residues of the “cold” extractions of sulphide concentrate WMS-1 (10 minutes, 30 minutes and 60 minutes) were analyzed by the strong extraction procedure of the GLIER analytical laboratory. This extraction consists of reacting the residues with a hot (100°C) concentrated nitric acid solution in sealed Teflon jars, for four hours. All metals, except those contained in refractory silicates and oxides are routinely put into solution by this technique.
4. Mercury analysis - Residual mercury in the CDE 2-extracted residues of anthropogenically contaminated sediment samples, with known mercury contents, were extracted by the CAEAL-accredited method used in the GLIER analytical laboratory.

A. Analytical Methods

5. Multielement analyses were carried out on extraction solutions that were variably diluted with 1% nitric acid into the working range of either the TJA, IRIS ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) or the TJA, PQ3 ICP-MS (Inductively Coupled Plasma Mass Spectrometer). Total method blanks were analyzed with each batch of samples.
6. Mercury concentrations were determined by cold vapor atomic absorption using a Varian SpectrAA.-300 with the VGA-76 vapor generation accessory.

RESULTS:

C. Reaction of CDE 2 with Geological Materials at Room Temperature (22°C)

A series of 5 CCRMP standard reference materials (SRMs) obtained from CANMET (NRCan) were chosen to represent a number of mining-related environments where CDE 2 might have applicability. These range from a massive sulphide ore (WMS-1) to slightly mineralized rocks (WGB-1, UM-1, UM-4) to ore tailings (UMT-1) and include materials used in the calibration of other leaching procedures (UM-1, UM-4). Descriptions of these SRMs, taken from several publications from the Canadian Government and elsewhere, are provided at the back of this report. These materials were reacted with the CDE 2 solution for variable times (10 minutes, 30 minutes and 60 minutes) at room temperature (22°C) to test both the efficiency of CDE 2 in extracting metals from these materials and examining the effect of increasing time on the extractions. All analytical data are provided in Table 1A.

Massive Sulphide PGE Material (WMS-1): The percentage of the total content (as certified for this material) of Copper (Cu), Nickel (Ni), and Cobalt (Co) in WMS-1 extracted by CDE 2 at room temperature for 10, 30 and 60 minutes, is shown in Figure 1. Copper (mean = 34%) has the highest extraction efficiency of the three metals followed by Ni (mean = 24%) and Co (mean = 17%). There is no strong trend of increasing extraction with time, although the 60 minute experiment had the highest Cu and Co extraction efficiencies.

Chalcopyrite (CuFeS_2) is the main copper-bearing phase in this ore whereas pentlandite ($(\text{Fe, Ni})_9\text{S}_8$) and pyrrhotite (Fe_7S_8) are the main Ni and Co bearing phases. The different extraction rates for the 3 metals clearly indicates that CDE 2 reacts with these main sulphide phases at different rates, chalcopyrite >>pentlandite, pyrrhotite. These conclusions are verified (see later section) by the experiment in which temperature of the reactions were changed for this same ore material. The fact that there is no strong trend of interaction with time (for the limited time range studied) also suggests that there is a portion of these ore minerals (either very fine grains or smeared coatings on other grains) in the samples that are almost instantaneously dissolved by CDE 2, while the rest of the material (coarser grains?) only reacts slowly.

Gabbro Rock PGE Material (WGB-1): The percentage of the total content of a number of metals extracted by CDE 2 at room temperature for 10, 30 and 60 minutes, is shown in Figure 2. Lead (Pb = 98%) and zinc (Zn = 101%) are essentially 100% extracted by CDE 2 although the decreased measured Pb extraction at 60 minutes may indicate that it precipitates from the CDE 2 solution (as lead sulfate?) as the dissolved sulfur builds up, over time. Note, however, (Table 1) that Zn and Pb are both at very low concentrations in this reference material. Cu (18%) and Ni (15%) show significant extraction into CDE 2 with Ni exhibiting a significant increase in extraction with time. Very little Co or Cr is extracted by CDE 2 in this material.

The rapid and apparently (very low concentrations therefore higher analytical uncertainties) complete extraction of Pb and Zn from this material is in keeping with the expected higher reaction rates of galena (PbS) and sphalerite ((Zn,Fe)S) which probably host the small amounts of Pb and Zn in this material (galena is reported as a trace mineral phase in WGB-1. The similar behaviors of Cu, Ni and Co to those observed for WMS-1 is consistent with the same assemblage of host minerals for these elements (chalcopyrite, pyrrhotite and pentlandite) in the two materials.

Ultramafic Ore tailings PGE Material (UMT-1): Large quantities of Cu and Ni are extracted by CDE 2 from this material (see Figure 3), indeed more Cu than is reported in this material was extracted, suggesting that the material is inhomogeneous for Cu and presumably Ni at the sample size used in these tests (1 gram). The higher efficiency for Cu than Ni is in keeping with the previously described test materials and the reported presence (see Description section) of chalcopyrite and pentlandite as well as weathering products of the processed ore, goethite which probably has incorporated Cu and Ni into it as well. Little Co is extracted by CDE 2 possibly because the small amount of it contained in this material is contained in more refractory phases (a large variety of spinels and iron/magnesium silicates) that CDE 2 does not react with.

Both Cu and Ni show increasing extraction with time for this material and CDE 2, as well as much higher fast extractions (10 minutes). This may indicate that the grain size of the Cu, Ni host minerals is on average smaller than the first two materials tested (WMS-1 and WGB-1) and/or a significant amount of the Cu and Ni in this material is in secondary weathering phases like goethite which CDE 2 is particularly efficient at extracting metals from.

Sulphide-bearing Ultramafic Rock (UM-1): Very little Cu, Ni or Co are extracted by CDE 2 from this material (see Figure 4). The percentages of each metal extracted (Co>Ni>Cu) are also the reverse of what was observed in the first three materials studied. Currently no explanations exist for this unexpected result. The possibility that the bottle that this material was taken from is mislabeled, is being checked.

Sulphide-bearing Ultramafic Rock (UM-4): Within experimental uncertainty, all of the Ni and Co certified to be contained in sulphide minerals in this material are extracted by CDE 2, whereas only about 50% of the Cu is extracted. Like for UM-1 the percentages of each metal extracted (Co>Ni>Cu) are also the reverse of what was observed in the first three materials studied. This effect must be related to a different mineral composition of

this material compared to the first three materials, but the description of the mineralogy of UM-4 does not provide details as to what sulphides are present in this material.

There is no strong evidence of a time relationship on metal extraction efficiency in UM-1, possibly because the sulphides contained in this material react almost instantly with CDE 2.

Summary of Results: CDE 2 extracts variable, but generally large, amounts of metals from a variety of sulphide mineral-bearing earth materials. There are clearly mineralogical effects that result in different extraction efficiencies at room temperature (22°C). Although some evidence exists for increasing extraction of metals with increasing contact time with CDE 2, most of the metals extracted appear to be released into solution very early in their contact with the CDE 2 solution.

It should be mentioned that sulfur is released as a gas phase from the CDE 2 solution-powder mixtures, as the distinct odor of SO₂ was observed when they were mixed. This may need to be addressed in any application of CDE 2 to sulphide bearing materials.

D. Analysis of residue of Massive Sulphide PGE Material (WMS-1) after leaching for variable times at room temperature

The residues from the timed leaching experiments of CDE 2 on WMS-1 were reanalyzed with the hot 50% nitric acid dissolution procedure. Analytical results are provided in Table 1A.

The correlation between the CDE 2 leached samples and the nitric acid results are good. The one CDE 2 leached sample of WMS-1 (WMS-1B 30 MIN) that showed low leaching rates had anomalously high concentrations of Co, Cu, Fe, Ni, Pb, V, and Zn in the residue, validating the first experiments results. Although it is difficult to quantify the results of this experiment the following results are clear:

- a. Ni is higher in the residue than the starting material demonstrating that although a significant amount of Ni is dissolved by CDE 2 its dissolution rate is less than that of the bulk sample.
- b. Cu and Co are dissolved at rates slightly faster than the bulk sample
- c. Zn (even though no certified values are reported for WMS-1) is dissolved much more quickly than the bulk sample suggesting that CDE 2 is very effective at extracting zinc from sulphide ores.

E. Reaction of CDE 2 with Massive Sulphide PGE Material (WMS-1), at variable temperatures

The massive sulphide material WMS-1 was used to test the effect of temperature on the ability of CDE 2 to extract metals from a complex ore material. One g of WMS-1 was reacted with 5 g of CDE 2, in triplicate, for 60 minutes at 30°C, 60°C and 90°C, respectively. The resulting leach solutions were analyzed for dissolved metals to determine the percentage of the total metals that were extracted at each temperature by

CDE 2. The analytical data is provided in Table 1A.

The percentages of Cu, Ni, and Co extracted from WMS-1 by CDE 2 in 60 minutes, at the three temperatures, are shown in Figure 6. Cu shows an almost perfect linear relationship between temperature and metal extracted between 30°C and 90°C whereas Ni and Co exhibit a much shallower slope as well as steepening slope in metal extracted versus temperature. It should be noted that in the initial experiments (Section A of RESULTS) described above an additional extraction for 60 minutes was done at room temperature (22°C) that is at variance with the trends observed in this experiment. The amounts of all metals extracted were much higher at 22°C than at 30°C (Cu 42% vs 8%, Ni 25% vs 12%, Co 18% vs 5%) and the order of metal extractions Cu>Ni>Co (22°C) became Ni>Cu>Co at 30°C. The initial order observed at room temperature was restored at the higher extraction temperatures. The initial experiments were performed shortly after the receipt of CDE 2 (end of February, 2001). This leaching experiment and those described below were performed at the end of June, 2001 using the same CDE 2 solution that had been sitting in the half-empty storage container for approximately 4 months.

Clearly increasing the temperature increases the extraction efficiency of CDE 2 for this material. The discrepancy between leaching results for the freshly received CDE 2 (February) and the leaching results for the same solution, which had been stored for 4 months (end of June) suggests that CDE 2 may lose some of its effectiveness with a long storage time.

D: Reaction of CDE 2 with metal-enriched sediments

Three metal-enriched sediments from the western basin of Lake Erie, two of which are proximal to a major environmental area of concern, were reacted with CDE 2 at room temperature (22°C) for one hour. The CDE 2 solution used in this experiment had been stored for over 4 months after original use and, as discussed in the previous section, had lost some of its original potency to leach metals. The data for these extractions are contained in Table 1B.

The amounts of metals extracted from the sediments by interaction with CDE 2 at room temperature are presented in Figures 7-9, as a percentage of the hot 50% nitric acid extraction used in the GLIER labs. For Cd, Cu, Pb and Zn, CDE 2 extracts >80% of the amounts of these metals that are extracted by the hot nitric acid technique from the contaminated sediments (8LE8 and 8LE7). Only Cu is slightly less efficiently extracted in the laboratory standard material S-CNT. Lesser amounts of Co, Cr and Ni are extracted by CDE 2 in all three sediments tested. This is in stark contrast to the hot aqua regia leach data provided for S-CNT (Figure 7). The CDE 2 leaching efficiency is lower for the Lake Erie reference material where only Cd and Pb are extracted at rates exceeding 80% of the hot nitric acid technique. Cu and Zn extraction efficiencies are between 60 and 80% while Co, Cr, Ni and V efficiencies are < 40%. Data for sediment matrix elements Al and K (representative of the clay and feldspar contents of these sediments) demonstrate that CDE 2 does not significantly leach the primary silicate material that makes up the bulk of these sediments. Ca (primarily present as aragonite shell fragments in these sediments) and Mg are strongly removed by CDE2 (as well as by a cold 5% acetic acid extraction). Fe and Mn are moderately to strongly extracted from the sediments with more extraction

seen for the two anthropogenically contaminated sediments than for S-CNT.

A direct comparison of the extraction efficiencies of CDE 2 for the three sediments is provided in Figure 10. CDE 2 extracts much higher quantities of metals from the two anthropogenically contaminated sediments (8LE7 and 8LE8) than from the more normal sediment S-CNT. This is true for all metals but is particularly so for elements of environmental concern - Co, Cr, Ni, V, Cd, Cu, Pb and Zn.

The CDE 2 extracted sediment residues from the above experiment were analyzed for mercury (Hg) to determine the quantity of Hg not removed by CDE 2. In all cases (Table 1C) only a trace of the original mercury (1.08 to 1.55 ppm) remained, and for the three samples tested 84.3% (range 83.0 - 85.3%) of the mercury originally contained in these sediments was removed by interaction with CDE 2.

Summary of Results:

CDE 2 strongly extracts metals of environmental concern from the fine grained sediments tested at room temperature. In particular the metals of most concern, Hg and Cd are very efficiently extracted. These results have been obtained with a CDE 2 solution that had been stored for a significant time and has been found to be less reactive with geological materials than freshly made CDE 2. Even the impressive results obtained above, do not demonstrate the true capability of CDE 2 to remove metals from highly contaminated sediments.

CONCLUSIONS:

1. The CDE 2 solution tested has the ability to leach major quantities of metals from sulphide-rich ores and ore tailings at room temperature (22⁰C).
2. The CDE 2 solution tested appears to react more rapidly with certain sulphide minerals at room temperature, resulting in the preferential leaching of Cu over Ni and Co, in most materials.
3. The CDE 2 solution tested leaches metals from a sulphide ore much more rapidly at elevated temperatures (60⁰C and 90⁰C vs 30⁰C) and the contained sulphide minerals have different leaching responses to the increased temperatures.
4. The CDE 2 solution tested appears to lose some of its reactivity when stored for long periods of time.
5. The CDE 2 solution tested is extremely effective at extracting a wide range of environmentally sensitive metals, at room temperature, from normal, as well as anthropogenically contaminated, sediments. It is particularly effective at removing the most environmentally toxic metals, Cd and Hg.

RECOMMENDATIONS:

1. Further testing and optimization, is required with CDE 2 for mining and mineral processing applications. Pure sulphide mineral separates should be used to generate fundamental data on leaching/reaction rates for different ore mineral species.
2. The effect of temperature on leaching rates of different sulphide minerals should be investigated further,
3. The degradation over time of the effectiveness of freshly made CDE 2 solution needs to be investigated.
4. Current test results of CDE 2's effectiveness at leaching metals from sediments (particularly Cd and Hg) suggest that applications for CDE 2 in the environmental clean-up industry should be investigated as a priority.
5. CDE 2's effectiveness at removing persistent organic pollutants (POPs) such as PCBs and polycyclic aromatic hydrocarbons (PAHs) from sediments along with the metals, as documented in this study, should be investigated to better evaluate the application of CDE 2 to other outstanding environmental cleanup issues.

REFERENCES:

Canadian Certified Reference Materials Project (CCRMP)

www.nrcan.gc.ca/mms/canmet-mtb/crmp

Cameron E.M. 1971. Three Geochemical Standards of Sulphide-Bearing Ultramafic Rock: UM 1, UM 2, UM 4. Geological Survey of Canada Paper 71-35.

DESCRIPTIONS OF SAMPLES USED IN CDE2 TESTING

A. CCRMP STANDARD REFERENCE MATERIALS

MASSIVE SULPHIDE PGE MATERIAL (WMS-1)

WMS-1 was obtained from the Wellgreen Complex, Yukon Territory Canada. This material is composed largely of sulphides rather than silicates. The sulphides in this material are massive in form, intimately associated with one another and composed of pyrrhotite with smaller quantities of pentlandite, chalcopyrite, minor sphalerite and galena. The massive sulphides contain inclusions of magnetite many of which are severely fractured and veined with silicates. Silicates form a much smaller portion of the material and include an iron aluminum silicate. Chlorite, mica and quartz.

ULTRAMAFIC ORE TAILINGS PGE MATERIAL (UMT-1)

UMT-1 is a sample of mill tailings from the nickel-copper Giant Mascot Mines, Hope, British Columbia. UMT-1 is composed almost entirely of silicates including pyroxene (enstatite), amphibole (tremolite) and chlorite. Ore minerals comprise a minor portion of the tailings, and include magnetite, ilmenite, goethite and some iron, magnesium, aluminum and magnesium spinels. Both sulphide species present, pentlandite and chalcopyrite, occur as liberated grains and as small inclusions in the silicates.

GABBRO ROCK PGE MATERIAL (WGB-1)

WGB-1 was obtained from the Wellgreen Complex, Yukon Territory Canada. The mineralogy of this gabbro rock consists of plagioclase feldspar, pyroxene, chlorite, prehnite and calcite. Sulphide mineralization in the sample is sparse and includes chalcopyrite, pyrrhotite, pentlandite and galena (intimately associated with pyrrhotite). Other minerals identified include titanite, ilmenite and rutile.

SULPHIDE-BEARING ULTRAMAFIC ROCKS (UM-1 & UM-4)

These rocks are intended as reference materials for the determination of ascorbic acid/hydrogen peroxide-soluble copper, nickel and cobalt in ultramafic rocks to evaluate their ore potential.

UM-1 is a peridotite from the Giant Mascot Mine at Hope, B.C. It consists of 80-85% olivine, 3-5% orthopyroxene, 5% augite, 5% pale yellow hornblende, 5-10% sulphides and 1% chromite. The primary high temperature mineralogy of the rock is little altered.

UM-4 is a serpentinized hornblende metaperidotite from the Werner Lake-Gordon Lake district of northwestern Ontario. The rock is composed of about 30% serpentine (after olivine), 55% pale hornblende, 10% hypersthene, 5% dark olive-green spinel and minor sulphides.

A. LAKE ERIE SEDIMENTS

LAKE ERIE REFERENCE SEDIMENT (S-CNT)

S-CNT is a very fine grained sediment from the western basin of Lake Erie, collected south of Colchester. It is the internal sediment reference material used by the GLIER analytical laboratory. Although it contains elevated metal concentrations compared to most Canadian lake sediments, its collection site is remote from known point sources of anthropogenic origin.

LAKE ERIE SEDIMENT 98-7

Sediment sample 98-7 is the fine grained fraction of a highly contaminated sediment collected near (approximately 5 km) the Michigan shoreline. This sediment contains a much higher proportion of its metal contamination in an easily extractable form, than typical for the western basin of Lake Erie (e.g. S-CNT)

LAKE ERIE SEDIMENT 98-8

Sediment sample is the fine-grained fraction of moderately contaminated

sediment collected farther away (approximately 10 km east of 98-7) from the Michigan shoreline than 98-7.