Soil chemical and mineralogical principles in rehabilitation of infertile copper mine tailings for growing crops in China

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Abstract
In China approximately 20,000 hectares of land are degraded each year by mining and lost to agricultural production or other valuable uses. Two copper mines at Yuanqu, Shanxi Province, and Tong Ling, Anhui Province, were selected as pilot projects for an AusAID-funded mine waste rehabilitation project. The tailings of these mines made an inhospitable environment for plant growth, with sparse volunteer weeds of a few species colonizing the Yuanqu tailings, and no plants colonising the Tong Ling site. The main soil deficiencies were: (a) complete absence of available P and very little available N, (b) extremely small water holding capacity, (c) close to zero organic matter and zero cohesion, (d) extremely small cation exchange capacity, and (e) alkaline pH due to large amounts of calcite and dolomite. In addition, the tailings contained significant concentrations of copper and cobalt, which were potentially of concern if the crops to be grown were to accumulate these to dangerous concentrations. We mixed the tailings with local loess, containing 35% clay, adding fertilizer, and experimented with green manures (sudax-lupins, white clover-perennial rye grass, mung beans) to amend the tailings and make crops grow. We also used geochemical theory to assess solubility of the heavy metals and predict their availability to crops. Good results were obtained with a range of crops: peanuts, sorghum, and winter wheat. The sudax green manure had a beneficial effect lasting beyond the first crop.

Key Words
Heavy metals availability and uptake, crop productivity, soil creation

Introduction
The Chinese and Australian Governments (AusAID) co-operated to mitigate environmental degradation from mine waste. The work was carried out by a Joint Venture of ACIL Australia Pty Ltd and Woodward Clyde Pty Ltd in cooperation with the Environmental Protection group of the Beijing General Research Institute of Mining and Metallurgy. Both partners fielded multi-disciplinary teams, but the Australian team also included a soil scientist.

The pilot areas for tailings rehabilitation were located at two copper mines, respectively near Yuanqu in the Zhong Tiao Shan mountains and at Tong Ling on the Yangtze River flood plain. The tailings contained residual copper and cobalt but insignificant amounts of other heavy metals. The aims were to enable productive cropping on the tailings at Yuanqu and to create grassed and treed areas for future urban use at Tong Ling. It was important to ensure that produce grown on the tailings did not contain hazardous levels of heavy metals. Dust suppression was a major issue at both locations. Development of a general rehabilitation capability for wider use in China was the ultimate goal. This paper deals with the Yuanqu pilot project.

The approach to rehabilitation was to characterise the chemical properties, mineral suite, particle size distribution, and moisture regime of the tailings in order to predict the main limitations for plant growth and human health. Human health may be affected by dust as well as heavy metals if the latter enter the food chain in excessive concentrations. For plant growth the limitations are the virtual absence of available nitrogen and phosphorus, and small water holding capacity.

Due to a lack of organic wastes to add to the tailings, as local farmers remove most from their fields as feed for farm animals and burn the rest, our aim was to stimulate plant growth through fertiliser application and allow root matter and plant debris to increase soil organic matter gradually.

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Methods
The entire approach was based on understanding the mineral suite and chemical properties of the material to be converted to productive soil, taking into account natural weathering processes and accumulation of organic matter over time. The biosphere, here the crops, were considered part of the pedological process, and biomass production was to be promoted as much as possible. However, for the Chinese partner the yields obtained and the costs of the rehabilitation were the main measure of success.

The tailings were predominantly very fine to fine sandy in texture (particle size from 0.2 to 0.02 mm) with less than 1.5% clay fraction. At Yuanqu they contained about 30% carbonate. The bulk mineral composition of the tailings as well as that of the clay fraction (less than 1.5%) was determined. In the bulk sample quartz, dolomite and feldspar were co-dominant, with muscovite sub-dominant, and calcite forming a minor constituent. Possible traces of pyrite and talc were identified. Although not identified by X-ray diffraction there were also other dark minerals in the tailings, which presumably contained iron. The clay fraction was dominated by chlorite, muscovite and vermiculite with minor and trace amounts of calcite, dolomite, feldspar and quartz. Physical and mineralogical analyses were carried out by the State Chemistry Laboratory (SCL) in Werribee, Victoria, and the CSIRO Division of Soils Laboratory in Adelaide, South Australia.

At Yuanqu plant-available potassium (Skene Method using 0.05 M HCl extract) in the tailings was around 360 mg/kg, and considered to be adequate for crops. Plant-available phosphorus (Olsen *et al*. 1954) was always below detection (<0.1 mg/kg). Total Kjeldahl Nitrogen ranged from 10 to 68 mg/kg, except for old tailings at the surface with a sparse weed growth which contained 127 mg/kg. Phosphorus and nitrogen were considered to be deficient. Tailings only a few years old were devoid of colonising weeds. pH values (1:5 H_2O) ranged between 7.5 and 7.7.

Total and EDTA-extractable heavy metals were determined in all tailings samples, but only total concentrations will be discussed in this paper. At both pilot locations the tailings contained between 200-600 mg/kg Cu, 50-150 mg/kg Co, and 5-35 mg/kg As, well as minor concentrations of Mn, Pb, Se and Zn, and very small amounts of Cd.

To overcome the lack of cohesion between the tailings particles, as well as the lack of a clay fraction, we quarried a loess deposit close to the rehabilitation site. In earlier rehabilitation works in the Zhong Tiao Shan area some older tailings ponds had been covered with 1 to 1.5 m of locally quarried reddish brown loess material, with a dominantly silty clay loam texture (34% clay), prior to release of the "re-made" land to farmers. A few samples of this material proved to have a cation exchange capacity of about 400 mmol(+)/kg and between 0.2-4.0% finely disseminated calcium carbonate and occasional gypsum crystals. It is understood that cropping on these rehabilitated tailings ponds was successful from the start.

However, covering tailings with such a thick layer of imported soil material entails major costs. We believed that success could be had with mixing some loess soil with the tailings. We chose three different ratios of tailings to loess soil and a control without loess soil.

An experimental area of approximately 100 by 100 m was selected on the tailings, covering a level area on the crest of the dam of the Mao Jia Wan tailings pond, and fenced. The area was smoothed by bulldozer and subdivided into 144 square plots of 5 by 5 m, separated by 1 or 2 m wide paths for access. In a third of these, 48 plots, imported loess soil was brought in and placed on top of the tailings at four levels, with a control receiving none, and the others receiving 15 cm, 30 cm and 40 cm thick layers. These tailings treatments are called T1, T2, T3 and T4 respectively. These treatments were intended to give tailings-to-loess ratios of 1:0, 1:1, 1:3 and 0:1 as the latter was too deep to mix with tailings. T4 resembled functionally the traditional method but used far less loess. Each of the treatment areas had 12 plots to be planted to four crops in three replicates.

Due to logistical constraints, all the plots with the one level of loess placement were adjacent to each other. After placement of the loess the soil was cultivated to the maximum depth achievable with ox-drawn ploughs and a small ride-on tractor, or with shovels by hand. The intention was to mix the surface loess layer with as much of the underlying tailings as was possible. The maximum depth of cultivation with the available equipment was about 30 cm. In treatment T2 additional tailings was brought in on top

of the loess to achieve a 1:3 mixing ratio. Based on the average calcium carbonate content of the tailings (30%), the loess (1.2%), and the mixed soils of T2 and T3, it was estimated that following mixing rations were actually achieved:
T1: Tailings only
T2: Loess:Tailings = 2:1
T3: Loess:Tailings = 2.8:1
T4: Loess only (40 cm deep over tailings)

Each area of the first mentioned T1, T2, T3 and T4 was planted to two leguminous crops - soybeans and peanuts - and two graminaceous crops - maize and sorghum. Each crop had three replicate plots.

The only fertilisers available locally were a complete NPK fertiliser, ammonium phosphate and ferric sulphate. All plots received the following in kg/ha:
Nitrogen N: 180
Phosphorus P: 239
Potassium K: 36
Sulphur S: 177
Follow up Nitrogen, N: 245

These application rates, representing twice the usual application rate used by farmers in the district, were intended to make up for the lack of nutrients in the tailings-loess materials. The use of ferric sulphate was strongly recommended by the local Agricultural Extension Service for new soils.

In addition, three green manure treatments were superimposed on other plots of the T1 (zero loess) and T4 (40 cm loess) treatments. These were a first season (summer 1994) planting of, respectively, sudax (a sorghum-Sudan grass hybrid) and lupins (*Lupinus sp*.), perennial rye grass (*Lolium perenne*) and white clover (*Trifolium repens*), and mung beans, sometimes referred to as Chinese lentils, (*Vigna radiata*), to be followed by cropping for winter wheat in 1994-1995.

Details on row spacing, seed spacing, germination and crop development are reported in unpublished project reports available from CARIM in Beijing.

Results

Crop yields

Although average rainfall in the Zhong Tiao Shan area is 630 mm per year, with most rain falling in summer, the summer of 1994 was reported to be the driest for 30 years. A rain gauge could not be installed until the following year. Early rains were good and all crops, including soybeans and maize, developed to full size and were subjectively measured as knee-high and head-high respectively at flowering time.

Follow-up rains did not arrive and the soybeans failed to set seed, while maize cobs appeared to be rather small. The same phenomena were observed on farm land in the surrounding district. Peanuts and sorghum, however, produced worthwhile yields of the same magnitude as occurred in the district, as shown in Table 1. The data are based on sampling the entire plots, calculating an average in kg per mu ($1/15^{th}$ hectare) and aggregating the results for the whole treatment.

At planting time there appeared to be some moisture already in the tailings and the loess. Possibly there was enough water to start the swelling of the seeds. On the 23^{rd} of May 1994, several days after planting finished, there was good rainfall and in treatments T1, T2 and T3 rapid germination was observed, but none could be seen in T4 until June 5^{th}. It is hypothesised that in a dry summer water was available at lower matric potential in the sandier substrates of T1 to T3 than in the silty clay loam of T4.

Sinclair and Serraj (1995) suggested that soybeans belong to a group of legumes which transports nitrogen as ureides from the roots into the above-ground plant and is unable to do so effectively under drought conditions. Peanuts belong to a second group which transports N as amides and is less sensitive to soil drying. They classed soybean as a legume particularly prone to yield loss under drought

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conditions. Lack of rainfall produced drought conditions and low soy yields overall, but in T4 any water that fell could be held by the soil better than in the sandier substrates, benefiting the soybeans slightly.

We believe that part of the variability between plot yields within the same tailings treatment and for the same crop is due to uneven fertiliser distribution. Weighed amounts of fertiliser were broadcast by hand by inexperienced farm labourers and at the time the uneven application was easily observed.

It can be seen that peanuts could yield as well as the district average on the tailings if only supplied with adequate fertiliser, suggesting that peanuts may not require much water. Sorghum is known to be a drought-resistant grain crop. It performed above expectations in T2. There is an apparent trend for yields to decline with an increase in loess content of the root zone, with T2 having the highest yields, with peanuts being the only exception yielding best in T3. A hypothesis that water became less readily available with an increase in clay content and too easily lost by drainage in the pure tailings as the summer progressed would seem to be an obvious explanation. Soil water monitoring by neutron probe did not start until the 1996 growing season so that soil moisture data after that date cannot explain prior results.

Table 1 details the yields of the summer of 1994, the winter wheat harvest of 8th June 1995, followed by the summer crops of 1995 and the winter wheat harvested in early June 1996. Winter wheat was planted on the entire experimental area and also received complete fertiliser at double the district practice. Table 1 also suggests that the green manures had an effect in raising yields. T1 with sudax/lupins yielded almost twice as much wheat as did T1 cropped in the previous summer, even though the lupin component was almost non-existent. The same sudax/lupins green manure on T4 also gave an improved yield. Perennial rye grass and white clover established very poorly; very few clover plants became established. This type of green manure therefore could not demonstrate any possible benefit. The mung beans green manure showed a very small, possibly non-significant beneficial effect.

On the T4 sudax-green manure area the yield of 1995-96 winter wheat was more than 50% greater than on the T4 without green manure cropping area. This suggests that the effect of the sudax green manure lasts at least two years.

Heavy metal uptake

Uptake of heavy metals by plants is governed by solubility in the soil water and hence by speciation. Since the root zone of the tailings and the amended tailings may be characterised as a generally oxidising and alkaline environment, the predicted species are (Hutchinson and Ellison 1992):

Cobalt	Solid phase (s) and suspended solid (ss)	$Co(OH)_2$(ss), Co_3O_4(s), and (Co_2O_3(s)
	Ionic forms	Co^{2+}, $Co_2(OH)^{3+}$
Copper	Solid phase	Cu_2O(s), $Cu(OH)_2$(s), $CuCO_3$(s)
	Ionic forms	Cu^{2+}, $Cu(OH)^+$, $Cu_2(OH)_2{}^{2+}$

Since the tailings, the amended tailings and the loess all have free calcium carbonate, it is likely that both metals commonly occur as carbonates in the solid phase. At alkaline pH the high concentration of OH^- ions will depress the concentration of the ionic hydroxide species.

Römkens (1994), researching the behaviour of copper in Dutch soils heavily dressed with pig manure, found that there was an interaction between dissolved organic carbon (DOC) and Ca^{2+} ions in the soil moisture resulting in a precipitation of DOC when Ca^{2+} concentrations increased. At zero calcium concentration the DOC concentration was about 120 mg/L and this decreased linearly to about 20 mg/L at a calcium concentration of about 90 mg/L. Copper in the soil solution appears to be largely complexed to DOC, so that with the increase of calcium in the soil solution there was a proportional decrease in dissolved copper.

The amended tailings will always have an excess of carbonate, but the concentration of Ca^{2+} ions in solution will depend on the concentration of CO_2 in the soil air, which will vary with the biological activity in the soil and the ease of gas exchange with the atmosphere. These concentrations can be estimated using known carbonate equilibria equations, but in any case it is safe to assume that dissolved calcium will not be limiting the precipitation of DOC.

Table 1. Crop yields from experimental plots (kg/ha)

	Tailings treatments				Green manure treatments superimposed on tailings treatments						Normal ave. Yuanqu District
	T1	T2	T3	T4	T1-GM Sudax	T1-GM mung	T1-GM Rye-clov	T4-GM Sudax	T4-GM mung	T4-GM Rye-clov	
Summer crops 1994											
Peanuts in shell	2353	2148	2716	1636							2250-3000
Sorghum grain	4588	8082	6702	4537	All plots covered with green manure crops						7500
Maize kernels	2408	4269	3986	3244							5100
soybeans	88	153	129	236							2250-2400
Winter wheat 1994-95	675	1275	1215	1455	1170	870	675	1845	1485	1290	3750-4500; 1500-1875 in 1994-95*)
Summer crops 1995											
Peanuts in shell	1698	0	0	0	np	np	np	np	np	np	Most farmers did not plant summer crops due to drought
Sorghum grain	np	np	np	np	np	np	np	np	np	np	
Maize kernels	0	0	0	0	990	866	0	0	0	0	
soybeans	np	np	np	np	np	np	np	np	np	np	
Winter wheat 1995-96	np	1437	1665	1257	np	np	390	1964	1021	1369	2250 in 1995-96

Note: np = not planted. *) = no rain at all after early May until wheat harvest. Summer crops germinated one month too late.

Applying this finding to the calcareous tailings rehabilitation, we predicted that it was most unlikely for crops to take up excessive amounts of copper from the root zone, particularly as over time organic matter contents must rise.

Baker (1990) describes the existence of copper in soils as being in six ‘pools’: soluble ions, soluble inorganic and organic complexes, exchangeable Cu, stable organic complexes, adsorbed Cu on hydrous oxides of Mn, Fe and Al, adsorbed Cu on the clay-humus colloidal complex, and crystal lattice-bound Cu. The copper in the tailings is likely to exist chiefly as the crystalline carbonate, malachite, and in the presence of an abundance of dolomite and calcite it will be stable.

However, as the tailings weather, iron oxy-hydroxide coatings are forming on the particles as evidenced by colour changes from light grey to yellow browns and rusty colours. These iron compounds should capture and immobilise Cu ions from the water phase.

Because of its siderophile nature, Co in the tailings may be present in iron- and manganese-bearing minerals substituting for Fe and Mn. This Co is not readily available to plants. The solid phase forms of cobalt are all very insoluble (Smith, 1990) and Co is expected to be immobile in alkaline environments. Co released by weathering may be sorbed by other soil minerals, especially Fe and Mn oxides. Adsorption of Co to MnO_2 is well documented by Gilkes and McKenzie (1988), and increases with pH (McKenzie, 1967). Thus, excessive uptake of cobalt by the crops grown on the amended tailings is not expected.

Table 2 summarises heavy metal contents in the soil and amended tailings in which crops were grown, as well as in the seeds bought locally for the experimental crops, and in the edible produce, the harvested grains, beans or peanuts. Note in Table 3 that uptake in the produce of Cu and Co appears to be unrelated to the concentrations of these metals in the T1 to T4 soil/tailings media. This is expected because their solubility is largely controlled by alkaline soil pH in these calcareous materials.

Table 3 also shows that Cu concentrations in the produce are very similar to those in the bought seeds, which presumably were grown on ‘normal’ soils in the district. The leguminous crops appear to have a tendency to take up much more Cu than the graminaceous crops. For Co, the produce contains 4-8 times as much of this metal than did the original seed. Again, the leguminous crops accumulate more Co than the grains.

Table 2 Copper and cobalt concentrations in experimental tailings soils (mg/kg)

	T1			T2			T3			T4		
	‘94		‘95	‘94		‘95	‘94		‘95	‘94		‘95
	Spr	Aut	Aut	Spr	Aut	Aut	Spr	Aut	Aut	Spr	Aut	Aut
Cu	330	320	270	290	240	320	230	190	350	32	29	60
Co	n.d.	91	80	n.d.	80	130	n.d.	64	130	n.d.	14	20

Spr = spring; Aut = autumn; n.d. = not done

Table 3 Copper and cobalt concentrations in bought seeds and produce seeds (mg/kg)

	Maize		Sorghum		Peanuts		Soybeans		Winter wheat	
	Cu	Co	Cu	Co	Cu	Co	Cu	Co	Cu	Co
Seeds bought	2.1	<0.03	5.3	0.14	14	0.12	17	0.41	n.d.	n.d.
T1	4	0.13	5	0.25	16	0.74	19	3.3	n.d.	n.d.
T2	4	0.12	5	0.32	15	0.61	20	2.8	n.d.	n.d.
T3	4	0.12	5	0.21	15	0.73	21	2.6	n.d.	n.d.
T4	3	0.18	5	0.44	14	0.41	19	2.7	n.d.	n.d.

In terms of published tolerable daily intakes (TDI) by humans, which are official Government standards in The Netherlands (Vermeire et al. 1991), Table 3 suggests that the daily consumption of about 0.6 kg of maize, or about 0.3 kg of sorghum, or 0.16 kg of peanuts would approximate the TDI for Co, but only a much smaller proportion of the TDI for Cu.

Given the rather dry climate of Yuanqu, and the fact that gypsum crystals still can be found in the loess, which pre-dates the last glaciation, it may be safely assumed that there will be minimal leaching and the lime in the rehabilitated tailings will be present for very long times. The heavy metals may be considered to be inert for the next several thousand years at least.

Soil changes

The trials have not been conducted long enough to detect increases in soil organic matter concentrations with certainty. However, the colour of the tailings, which was originally various shades of grey, has become darker under cultivation. This may be due to increasing organic matter and formation of dark-coloured oxide iron and manganese coatings on the sand particles.

In the T1 plots, the organic matter concentration of a single sample of old tailings with sparse weed growth was 1.4% when cropping began in Spring 1994. It appeared to have risen to 2.1% by October 1995. However, only limited samples have been taken and the trend is not well established. While field data on organic matter accumulation in the plots are too few, it is expected that this process will follow a similar rate as that recorded by Crocker (1960) for soil deposited by mudslides in the north western United States, which indicated that the main accumulation of organic matter took place in the first six decades. Unfortunately, no further measurements of soil organic matter could be conducted at the end of the project in 1997.

The loess soil on the T4 plot had between 0.6 and 0.8% organic matter in Spring 1994. No further samples were taken.

Available soil phosphate levels in the tailings were always less than the detection limit (0.1 mg/kg), and about 0.2 mg/kg in the loess. In October 1995 in the fertilised plots these had risen to 5.5-7.6 mg/kg in T1 plots, 9.4 mg/kg in T2 plots, 10.6 mg/kg in T3 plots and 22-26 mg/kg in all T4 plots. It is possible that the high concentration of carbonates in the T1, T2 and T3 plots, inherited from the tailings, is reducing the availability of P compared to the loess.

Conclusion

Soil chemical and mineralogical theory is helpful in setting out an effective rehabilitation strategy for raw mineral tailings. Even though such theory is semi-quantitative to qualitative in field applications, it provides direction to strategy and certainty of final outcomes which purely empirical approaches cannot provide. Theory is applicable under any field condition, whereas empiricism can lead astray in new environments.

This experiment, with a limited budget for laboratory analyses, was intended by the Australian funding body to be a demonstration project, rather than a research project. In this respect it succeeded. As a strict research project it did not satisfy the requirements of statistical design and analysis, but it did demonstrate that rehabilitation is more than earth moving and sowing seeds of native vegetation. The Chinese partner saw it as a means of building up confidence of local staff, which it did. One year into the project, on October 1st 1994, the Chinese Government awarded the Joint Venture the Foreign Expert Friendship Award on the occasion of the 45th anniversary of Socialist Government.

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