Elemental and mineralogical composition of metal-bearing neutralisation sludges, and zinc speciation – A review

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ABSTRACT

Zinc (Zn) in sludges from neutralisation of acidic emissions is a potential environmental pollutant and an element of interest for recovery. Findings regarding the elemental and mineralogical composition of such wastes were aggregated from the literature and examined together for a better understanding of management options, with a focus on Zn. Zn concentrations ranged from 0.006-22% in 46 acid mine drainage sludges, 0.009%-43% in 72 metal-finishing sludges, 0.024%-11.5% in 32 pyrometallurgical sludges, and 1.71-55.7% in 14 Zn production sludges. The main mineralogical characterization technique was X-ray diffraction, which found the dominant minerals to be calcite, gypsum, quartz, and iron oxides, but could not identify considerable proportions of amorphous phases. More than 60 mineral phases were observed. Crystalline Zn compounds identified included oxides, hydroxides, sulfates, sulfides, and metallic Zn; spinel, olivine and carbonate dominated in pyrometallurgical sludges. Zn may also be present in crystalline phases of low concentration, solid solution, and/or amorphous phases, which could be identified and characterised in more detail using other techniques. Overall, it is concluded that Zn occurs in high concentrations and includes phases that have high potential environmental mobility. Zn recovery seems feasible and would also enable harmless disposal of the residual.

Keywords: high-density sludge; electroplating, galvanic, neutralisation, pickling, plating, hot filter cake, cold filter cake, industrial sludge, aluminium anodisation sludge

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1 Introduction

Sludges and filter cakes containing zinc and other metals are by-products from neutralisation of acidic wastewaters and dewatering of the resulting sludges. They arise from mining, metal (both pyrometallurgical and hydrometallurgical) production, metal-finishing, and other assorted industrial processes, such as centralised mixed industrial waste treatment and soil washing. Such sludges are usually classified as hazardous wastes, due to their high concentrations of toxic metals, including Zn, Cr, Cu, Ni, and Pb, which may leach out and pollute the environment. The conventional approach for managing these wastes is landfilling, often following stabilization/solidification[1-13].

More resource-efficient management of sludges, especially recovery of the metals they contain, has also been considered. Metal extraction and recovery methods[14] include oxidation[15,16], sulfidation[17,18], and other hydrometallurgical[19-33] methods (also with ultrasonic[34], microwave[35] and electrokinetic[36-38] enhancements), and pyrometallurgical[39,40], and hybrid[41-43] treatments. Although the recovery approach decreases heavy metal pollution, the remaining sludge remains a disposal problem. Accordingly, some have studied thermal treatment of sludges to produce glass[44-49], ceramics[50-58] (including M-type hexaferrite[59], keramzit[60], and bricks[61,62]) and cement clinker[63], with the intention of simultaneously consuming sludge, providing a necessary raw material, and retaining heavy metals[44-47,50-53,56,59-68].

Important chemical properties of sludges for their treatment and utilization include element concentrations, mineralogical phases, and chemical speciation of elements of interest. An understanding of these aspects is necessary to assess potential mobility of pollutants in the environment[69], and to develop the most efficient and environmental-friendly metal recovery and waste treatment processes. It is also needed for appropriate government regulation of waste treatment and other management. Therefore, this article aims to systematically review and critically analyse previous studies on the elemental composition and mineralogy of sludges. Zn has been chosen as a focus because it can be found in many sludges and is of interest for both recovery and as a potential pollutant. Since the amount of information on Zn speciation in sludges is limited, the review includes consideration of other techniques that could be used in further work.

2 Literature Review Method and Structure

2.1 Scope of the study

The European List of Waste[70] codes for the metal-bearing hazardous waste sludges from inorganic industrial processes investigated in this review are listed in Table 1. These sludges are classified into four major groups: acid mine drainage sludge, metal-finishing sludge, pyrometallurgical sludge, and Zn hydrometallurgical production sludge.

Acid mine drainage sludge (01 03 07* in Table 1) is generated from the neutralisation treatment of acidic leachate contaminated with metals. The acidic leachate arises when sulfide minerals in host rock (waste rock and tailings) are oxidized by air and microbiological activity in and around mines[71]. Zn production sludge is generated as a by-product from similar processing of acidic solutions as part of hydrometallurgical production, e.g., electro-winning of Zn (11 02 02* in Table 1). Metal-finishing sludge (11 01 09* in Table 1) refers to the by-product from neutralisation treatment of acidic wastewaters from processes such as electroplating, anodizing, coating (phosphating, chromating, and colouring), chemical etching, galvanizing, pickling, and electroless plating. Pyrometallurgical sludge (10 02 13*, 10 03 25*, 10 04 07*, 10 05 06*, 10 06 07* and 10 08 17* in Table 1) is the by-product from wet scrubbing of stack gas from thermal production of steelmaking, zinc, copper, and other metals[72], usually with hydrated lime, to remove SO_2 and particulate matter[73,74].

Most of the information about pyrometallurgical sludges in this review is for sludge from steelmaking, with some information for sludges from other metal metallurgical processes, Most of the information about Zn production sludge is for Zn hydrometallurgical processing, but there are a few data for mixed hydro- and pyro- metallurgical processing. The reviewed metal-finishing sludges primarily originate from galvanising and electro-plating processes.

Table 1 European List of Waste codes for hazardous industrial wastes investigated in this review[70]

Sludge type	**European *List of Wastes code*[70]**	***UK generation (tonnes in 2018)*[75]**
Acid mine drainage sludge	01 03 07*	60
Steel sludge (including basic oxygen furnace off gas sludge, blast furnace sludge, Linz-Donawitz sludge) (pyrometallurgical sludge)	10 02 13*	50,000
Aluminium thermal metallurgical sludge (pyrometallurgical sludge)	10 03 25*	5
Lead thermal metallurgical sludge (pyrometallurgical sludge)	10 04 07*	0
Zinc thermal metallurgical sludge (pyrometallurgical sludge)	10 05 06*	0
Copper thermal metallurgical sludge (pyrometallurgical sludge)	10 06 07*	0
Other non-ferrous thermal metallurgical sludge (pyrometallurgical sludge)	10 08 17*	0
Metal-finishing sludge (from electroplating, pickling, etching, anodising, zinc coating, phosphating, and alkaline degreasing)	11 01 09*	15,000
Zinc hydrometallurgical production sludge (including leaching filter cake, hot filter cake, and cold filter cake)	11 02 02*	110,000
Sludge from mixed industrial wastewater treatment	19 08 11*	200

2.2 Literature collection and selection

A search of the English language peer-reviewed literature was conducted initially using protocol-driven search strategies with the electronic databases Scopus, Web of Science, and Google Scholar, also using a “snowballing” approach[76]. The keywords used in the search were ‘acid mine drainage’, ‘acid rock drainage’, ‘anodising’, ‘blast furnace’, ‘basic oxygen’, ‘electroplating’, ‘heavy metal or metal’, ‘finishing’, ‘galvanic’, ‘industrial and/or industrial hazardous’, ‘metallurgical’, ‘neutralisation or neutralised’, ‘pickling’, ‘plating’, ‘phosphating’, ‘steel’, ‘sludge dewatering’, ‘(aluminium/copper/lead/ zinc) thermal pyrometallurgical’, ‘zinc’, ‘zinc hydrometallurgical production’, ‘zinc plating’, ‘zinc plant’ combined with filter cake, pressed cake, or sludge. These keywords were also entered as search strings into the Google search engine, to seek non-academic data about the wastes of interest, e.g., from government and industrial research reports.

The titles, key words, and abstracts of the papers yielded by the keyword search were reviewed, and 165 papers relevant to our review topic were selected for deeper reading. This led to the collection of information regarding element concentrations, sludge mineralogy, and/or Zn speciation from 116 papers. Figure 1 summarises the systematic literature review process, and the sources of information found at each stage.

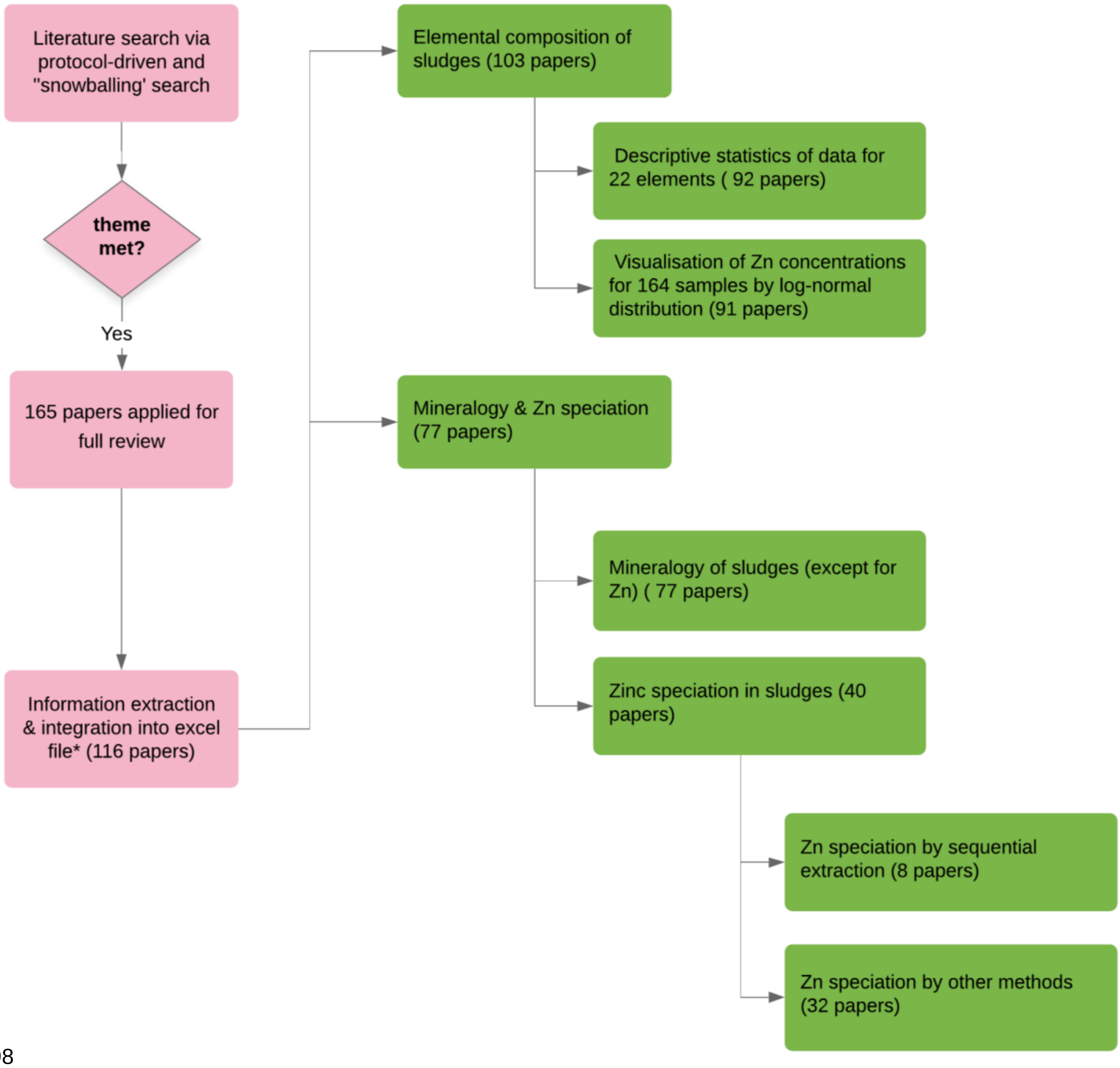

Figure 1. Flow diagram of review process. The steps for selection of papers are shown in pink and the resulting groups of results are shown in green (* The collected data and their sources can be seen in Appendix A).

2.3 Structure of the study

The information collected from the literature focuses on six aspects, which are discussed in the following sections. Section 3 gives a brief overview of how sludges are produced. Section 4 summarises and discusses the chemical and mineralogical analysis techniques that were used. Section 5 summarises element concentrations in sludges with a basic statistical analysis to help understand their variability, and log-normal probability distributions for Zn concentrations in particular. Section 6 describes the mineralogical phases found in sludges. Since the chemical form of an element, including its oxidation state, and binding to, or complexation with, other elements, plays a significant role in determining its behaviour and potential ecological impacts[77,78], Section 6 also discusses Zn speciation in sludges.

3 Generation and Management of Sludge

Figure 2 depicts the typical neutralisation process reported in the reviewed literature[6,22,42,51,52,79-81], in which acidic metal-bearing wastewater undergoes a series of physical-chemical treatment operations, to generate a mildly alkaline sludge. If highly soluble and toxic Cr^{6+} is present, the first stage is usually its reduction, still under acidic conditions (pH=2-3), through the addition of sodium bisulfite ($NaHSO_3$), sodium sulfide (Na_2S), or iron(II) chloride ($FeCl_2$). This is followed by neutralization with sodium hydroxide (caustic soda, NaOH), calcium hydroxide (hydrated lime, $Ca(OH)_2$, and/or calcium carbonate (manufactured precipitated calcium carbonate, $CaCO_3$, or limestone, which may also contain $MgCO_3$). The precipitation process generates a large amount of suspension, which may require coagulation and flocculation stages by adding aluminium, magnesium, or iron salts (e.g., $Al_2(SO_4)_3$, $MgCO_3$ or $FeCl_3$) and a high molecular weight anionic or cationic polymer, separately, before sedimentation. The high water content (typically >80%) of the sedimented sludge is usually decreased by filter-pressing, to reduce storage and transport costs. Even after filter-pressing, the water content of the sludge is typically greater than 60% (e.g., the water contents of 41 sludges reported in the reviewed literature ranged from 15% to 97%, with an average of 67%). The water remaining in the sludges is mainly 'bound water', which refers to vicinal water on the surfaces of solids, water of hydration, and water captured in the interstitial spaces. Only free water and some of the interstitial water can be removed mechanically (i.e., by filter pressing), which makes sludge dewatering difficult[82,83]. This typical treatment process may be modified depending on the situation, e.g., to selectively precipitate particular elements.

Three types of Zn-containing by-product sludge were reported in the reviewed papers on Zn hydrometallurgical production, which arise from leaching and purification of the primary Zn electrowinning production stream[23,26,30,33]. The first is a gypsum-based sludge with relatively minor Zn concentrations from hydrated lime neutralisation of the extract from concentrate leaching, mainly to remove iron. The second arises from oxidative precipitation of cobalt by adding $KMnO_4$ and hydrated lime, which has a high Zn concentration (hot filter cake). The third is precipitated when zinc powder is added to oxidise and remove nickel and cadmium by cementation, also with a high Zn concentration (cold filter cake). Sludges studied in four papers arose from zinc metal production using leaching following a roasting process.

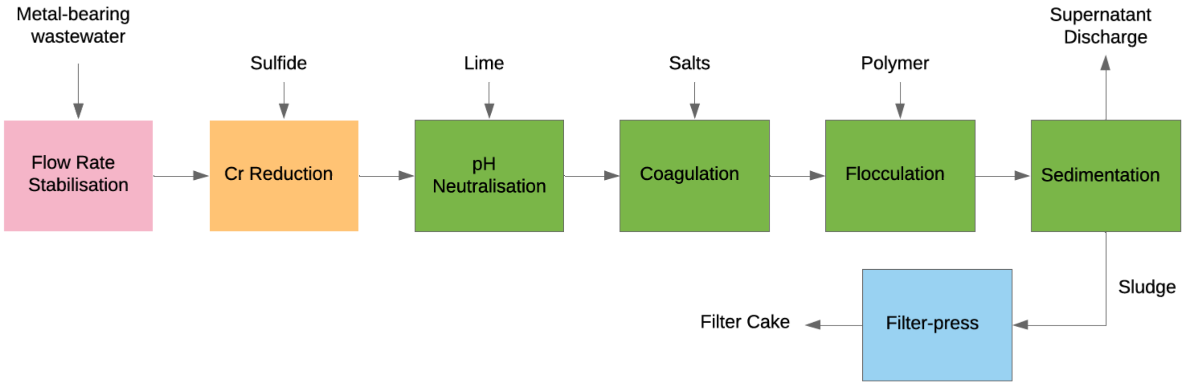

Figure 2. Typical sludge generation process (box with gold colour is pre-treatment and boxes with green colour is precipitation processes)

4 Characterisation Methods

This section compares the instrumental techniques used to determine element concentrations, sludge mineralogy, and Zn speciation. The toxicity of a sludge is related to the concentrations of toxic elements and, more significantly, their mobilities. Forty-four of the 86 reviewed documents used X-ray Fluorescence (XRF) to determine element concentrations in solid samples that had been dried at 100-110 ℃. XRF can investigate a wide range of elements at concentrations of percent to ppm with minimal dilution[84]. Its sensitivity has improved in recent decades to be similar in some circumstances to that of inductively coupled plasma (ICP) optical emission spectrometry (OES), which was used in 22 of the data sources. By convention, element concentrations are reported as oxides, though they usually have a more complex speciation. In general, the sensitivity of atomic spectrometric techniques is still higher, with the lowest detection limits being obtained by graphite furnace-atomic absorption spectroscopy (AAS) and ICP-mass spectrometry (MS). AAS was used in 17 of the data sources, and ICP-MS in 3 of the data sources[85,86]. Spectrometric techniques however require acid digestion of the solid samples, for measurement of element concentrations in a liquid sample, and detection limits can be affected by interferences with other elements, especially since considerable dilution may be required. Depending on the digestion method, some phases may not be dissolved. In the case of Zn, refractory phases, such as chromite, can contain zinc that may then be missed in the analysis.

Toxicity and mobility of toxic elements are also linked to their chemical speciations[87,88]. Element speciation is related to the bulk sludge mineralogy that hosts the toxic elements, either through solid solution in, or sorption to, the main phases, or as separate phases with a composition influenced by the bulk matrix composition. Sequential chemical extractions use progressively more destructive reagents to digest the solid phases, followed by spectrometric analysis, and then speculate about the speciation of elements based on their partitioning in the different fractions[89-91]. The basic method has been adapted by many different authors, but the operationally defined fractions are generally listed in order of decreasing mobility: water soluble, ion exchangeable, carbonates, associated with Fe-Mn oxides, bound to organic matter, and residuals, which are usually aluminosilicate minerals. However, this extraction method may destroy the initial chemical state, has poor reproducibility[88,91], and fails to identify the specific and spatial speciation at a molecular level.

Instrumental investigations of sludge mineralogy and speciation of elements often use powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). Although XRD is simple to operate and fast, its technical basis on diffraction of X-rays by a crystal lattice means that it cannot be used to probe amorphous phases[41,92-95]. Furthermore, minerals must represent more than 2% of dry sample mass[41,94,95] to be reliably detected. SEM can be used to identify the physical form (morphology, crystallinity), size and distribution of phases, and energy dispersive x-ray spectroscopy (EDS) is used to identify elements. Together, information about morphology and elemental composition may be used to postulate phases. Automated image analysis of SEM photomicrographs informed by EDS (e.g., QEMSCAN) can then be used to quantify the postulated phases. But such automated mineralogy cannot discriminate between minerals with similar spectra (e.g., hemimorphite/willemite)[96] and the detection limit for bulk mineralogy is about 3%[97]. Since the areas examined are very small, numerous analyses are necessary to ensure that they are representative of the whole material. ^{57}Fe Mössbauer spectroscopy was only found in two papers, where it was used to detect oxidation state, local coordination, and the magnetic state of the Fe-Zn phases in the sample. This technique is useful for investigation of speciation of iron, but it is limited to elements with suitable isotopes[98]. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) spectrometry were also applied.

Vespa, et al. [99] argue that X-ray absorption spectroscopy (XAS) is one of the few techniques for direct molecular-level studies of specific elements (e.g., Zn) in complex materials with low crystallinity. This technique has relatively low detection limits (100 mg/kg for bulk analysis and 10 mg/kg for micro-focused investigations), can be used on non-crystalline samples, and requires minimal sample preparation[88,98,99]. Besides, compared with other spectroscopic methods, XAS is applicable without the need for specific spin states or isotopic substitution[100].

An explanation of XAS, including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analysis, can be found in many research papers[88,99,101]. While EXAFS involves single scattering of the electron from the absorbing atom, the origin of XANES is more complex and includes several processes. XANES can provide information about the electronic structure, oxidation state, and coordination state, etc., while EXAFS primarily provides information regarding coordination number, distances, and species of the neighbours of the absorbing atom. At a basic level XANES can be used as a “finger-printing” method to identify the speciation of an element by comparing with relevant standards. The main drawback of XAS is that interpretation of the spectrum depends on availability of appropriate reference spectra and/or crystallographic information, which may not exist for impure systems, e.g., solid solutions. Zn can have a coordination number of four to six. Zn minerals with combined coordination, poor crystallinity, and/or impurities result in spectra that are hard to fit[102]. Additionally, XAS requires access to uncommon synchrotron radiation facilities[98].

5 Elemental Composition

5.1 Overall composition

Elemental compositions of sludges found in the literature and descriptive statistics are summarized in Table 2. Since the distribution of chemical analytical data is typically log-normal, geometric means and geometric standard deviations were calculated for the logarithms of the data[103]. For log-normal data, the standard deviation is multiplicative, rather than additive. For example, for a population of aluminium data with a geometric mean concentration of 0.938% and a geometric standard deviation of 6.86, ~68% of the data lie within the range from 0.14 to 6.4% (i.e., 0.938 x/÷ 6.86). The skewness calculated for the log-normal data is close to zero for most elements, which confirms that this was an appropriate assumption.

After deducting the elements with less than 10 analyses reported in the reviewed papers, 21 elements remained, with 13 to 150 analytical results for each. The total sample number collected was 161, and data below the detection limit (reported as 0 or ND) were not included unless the detection limit was reported. The composition of the sludges was thus revealed to be remarkably complex. Most of the analyses were for metal-finishing sludges (47%), followed by acid mine drainage (32%), pyrometallurgical (14%, of which 57% were from steelmaking), and Zn production (7%) sludges. Oxide compositions were converted into elemental compositions, and elemental concentration data with different units were all converted to % dry mass, reported to two significant figures.

Table 2 shows that the median concentrations for most elements are close to their geometric means, except for the median Al, Ca, Cl, Cr, Cu, Fe, Ni, and Sn values, which are around 1.5 times of their geometric means, and Mn and Ti, which are about half. This effect is also illustrated by their relatively large negative and positive skewness values (marker '°' in Table 2). Thirteen elements were found at median concentrations greater than half a percent:

- The toxic metals, Cr, Cu, Ni and Zn, are elements of industrial interest and/or impurities in the relevant industrial processes, including metal mining, production, and finishing.
- Ca and Na originate from the neutralisation/scrubbing reagents, and Na may also arise from sulfide reduction.
- Al, Fe, Mg, and/or Si may have been added in sludge coagulation, or may have a geological origin, especially in acid mine drainage and pyrometallurgical sludge, but also in industrial reagents.
- The main sources of S and Cl are likely to be the sulfuric or hydrochloric acids that were neutralised, though they may also have been added in reduction or coagulation reagents.

Large geometric standard deviations were found for As, Cd, Cl, Co, Cr, Cu, Ni, P, Pb, and Zn (marker '*' in Table 2), reflecting the wide ranges of concentrations of these elements in the sludges.

5.2 Concentration of Zn

For a better understanding of the variation of zinc concentrations in sludges from different sources, the Zn data collected for 164 sludges are plotted as log-normal probability plots in Figure 3. In normal probability plotting, the cumulative frequency distribution of the data is mapped onto a plot with an ordinate whose scale is adjusted such that data that are normally distributed fall in a straight line. The ordinate shows standard deviations from the mean, which correspond to a probability of the normal distribution[104]. The Zn concentration range can be observed to varyfor different sludges: 0.006%-22.0% in 46 acid mine drainage sludges, 0.009%-43.0% in 72 metal-finishing sludges, 0.024%-11.5% in 32 pyrometallurgical sludges, and 1.71%-55.7% in 14 Zn production sludges. The respective geometric means for the different sludges are 0.36%, 2.25%, 1.27%, and 18.1%, with similar medians of 0.66%, 3.17%, 1.76%, and 19.8%.

Although all four of the plots for the different sludge types show some curvature of the trend indicating a deviation from a strictly log-normal distribution, this is fairly slight for all but acid mine drainage sludges. A relatively convincing straight regression line (R=0.96) is evident for the log-normal probability plot of Zn concentrations in metal-finishing sludges. A small group slightly above the line on the right indicates lower concentrations measured for zinc plating or galvanising operations than expected based on the trend; this observation may be attributable to the optimisation of these processes for using Zn efficiently. No obvious reason for the divergence of four outliers from the linear trend at the lower end of the concentration range could be identified. The Zn contents associated with Zn production sludges also suggest a straight regression line (R=0.95), but a smaller number of data points makes it difficult to be sure of the distribution. The Zn concentrations in acid mine drainage sludges fall into three main groups. A Zn content of less than 0.14% is mainly associated with coal mine drainage sludges; this is consistent with zinc in coal mine drainage sludge being below detection by XRF, as reported by Marcello, et al. [56]. Mine drainage sludges from metal, especially Pb-Zn, mines tend to have Zn contents larger than 5.0. The middle group ranging from 0.14% to 5% is dominantly contributed by simulated acid mine drainage sludges or other metallic mine sludges (Ag, Cu, Au/Cu/Ag). For the sludges from pyrometallurgical gas treatment, the slope of the log-normal distribution for Zn concentrations above 1.1% is steeper than that for the population with lower concentrations. However, no clear relationship between these trends and the sludge sources could be identified.

The full collection of Zn concentrations (shown in the top left of Figure 3) visibly diverges from the log-normal distribution, mainly due to the inclusion of the acid mine drainage sludge data. Yet the general trend (regression coefficient R=0.97) is useful information in developing policies and technologies for the management of these sludges.

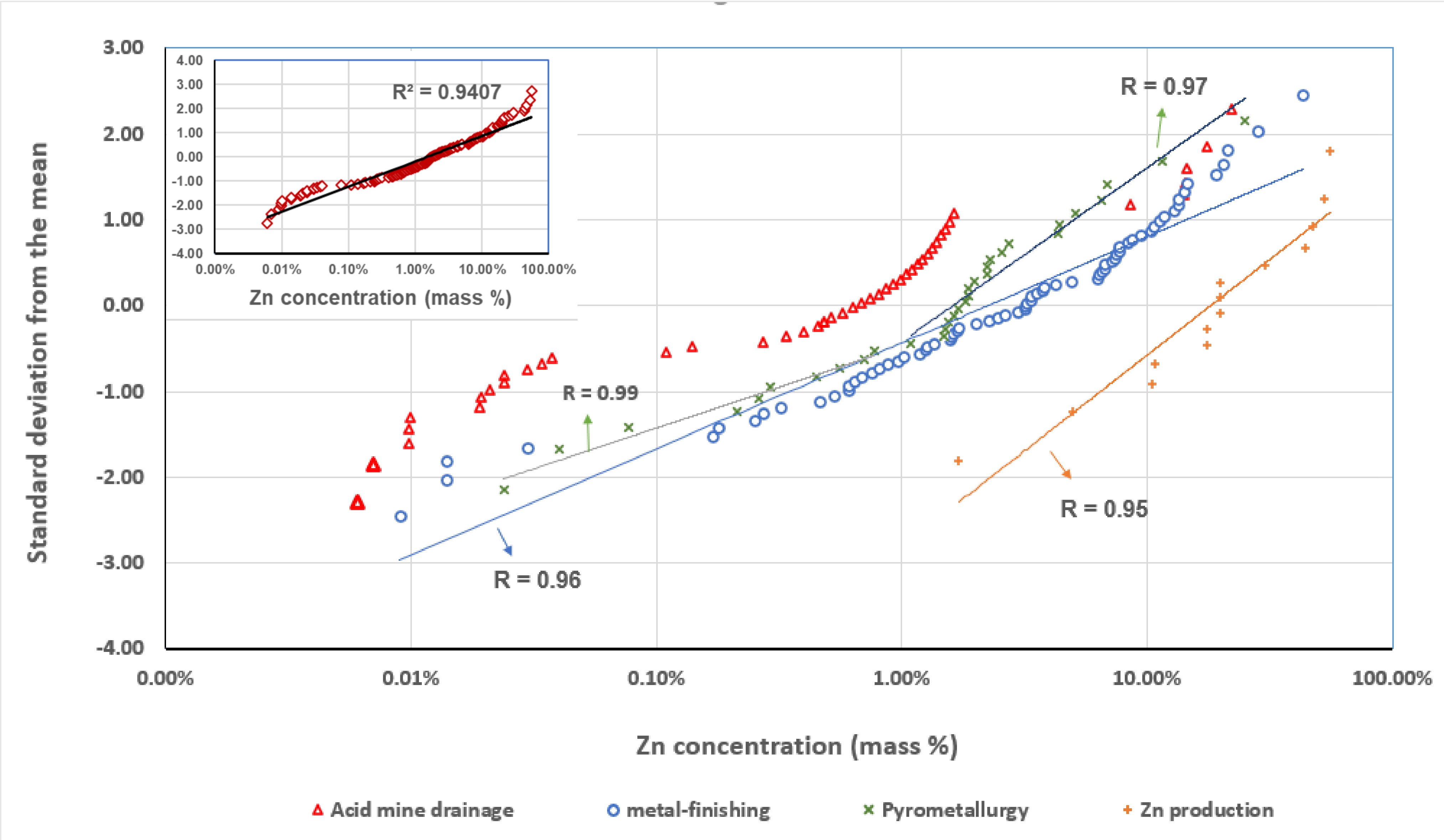

Figure 3. The cumulative log-normal distributions of Zn concentration in four types of neutralisation sludges. Lines represent the regression fit for each; a regression line for acid mine drainage sludges is not shown since a log-normal trend is less apparent. The log-normal distribution of the Zn concentrations in all sludges is plotted in the top left. The references for Figure 3 are collected in Appendix A.

Table 2 Element concentrations (% dry mass) in sludge analyses from the literature (sources in Appendix A)

Element	Minimum	Maximum	Median	Geometric mean	Geometric standard deviation	Skewness	Number of Sludges				
							Acid Mine Drainage	Metal-finishing	Pyro-metallurgical	Zn production	Total
Al	0.00007	35.4	1.31°	0.938°	6.86	-1.17°	46	52	19	3	120
As	0.0002	15.9	0.030	0.054	36.7*	0.11	12	5	7	5	29
Ca	0.014	40.6	7.43°	4.51°	5.33	-1.37°	46	59	27	9	141
Cd	0.000004	9.02	0.012	0.010	34.8*	-0.44	21	13	9	10	53
Cl	0.0001	8.82	0.740°	0.463°	17.4*	-2.33°	1	11	1	0	13
Co	0.0002	3.10	0.013	0.020	19.3*	0.15	6	11	0	9	26
Cr	<0.001	28.5	1.37°	0.737°	12.3*	-0.70°	6	60	2	1	69
Cu	0.0003	60.2	0.416°	0.253°	18.4*	-0.45°	41	63	7	9	120
Fe	0.002	74.0	7.71°	5.44°	6.37	-1.04°	46	70	21	13	150
K	<0.0002	7.20	0.137	0.117	6.08	0.77	13	28	8	1	50
Mg	<0.012	13.7	0.635	0.535	5.42	-0.79	44	30	21	8	103
Mn	0.001	27.9	0.155°	0.200°	9.06	0.58°	31	29	15	7	82
Na	0.002	9.57	0.568	0.456	4.95	-0.77	26	38	10	2	76
Ni	<0.0005	36.0	0.500°	0.295°	14.9*	-0.56°	9	60	1	11	81
P	0.004	19.8	0.400	0.327	13.2*	-0.27	13	27	5	1	46
Pb	<0.0002	16.2	0.080	0.086	14.9*	0.11	13	35	19	12	79
S	0.024	14.1	2.97°	2.20°	4.40	-0.83°	33	29	15	3	80
Si	0.001	39.8	0.868	0.809	6.25	-0.69	31	41	14	1	87
Sn	0.0007	3.76	0.660°	0.305°	5.88	-1.80°	1	16	7	1	25
Ti	0.003	3.54	0.035°	0.056°	5.09	0.96°	14	11	3	4	32
Zn	0.0003	55.7	1.99	1.46	10.0*	-0.99	44	67	26	13	150
				Proportion of total sources (%)			32	47	14	7	100

6 Mineralogy

6.1 Sludge Mineralogy

The mineral phases previously found in metal-bearing neutralisation sludges are summarized in Table 3. The reported phases vary markedly with different sources and treatments of sludge.

Fifty-five acid mine drainage sludges, 37 metal-finishing sludges, 17 pyrometallurgical sludges, and 11 zinc production sludges were examined mainly by XRD, SEM-EDX, with a few investigations by XPS, geochemical modelling, ^{57}Fe Mössbauer spectroscopy, or XAS. The crystallinity of all of the sludges was found to be low [1,8,15,19,29,30,44,46,53,54,59-61,65,66,71,93,95,105-117], but a wide variety of phases were identified. Eight papers reported that the sludges were composed of fine amorphous particles containing heavy metals, without any observation of crystalline minerals by XRD[18,46,53,59,60,65,107,118-120]. Chen and Zhou[107] reported that even thermal sintering failed to increase the crystallinity but provided little detail about their findings. The loss on ignition measurements for the sludges follow a normal distribution ranging from 7 to 47% with a mean of 27%, standard deviation of 8.24, and a skewness of 0.08. Results from two sources that conducted thermal analysis[67,76] suggest that loss on ignition was mainly due to free and combined water (lost below 200°C), but it also included dehydration of metal hydroxides, and decomposition of carbonates and sulphates, and could have included loss of organic matter (e.g., due to polymer addition for flocculation/dewatering).

The dominant crystalline phases in acid mine drainage and metal-finishing sludges were found to be $CaCO_3$, usually calcite, but in one acid mine drainage sludge, dolomite[121], in one aragonite[108], and in another both[122]; and calcium sulfates, usually gypsum, but also hemihydrate and anhydrite. The most common neutralisation reagents, lime and portlandite[68], were only detected in a few samples, suggesting that they were consumed in the neutralisation reaction or carbonated by exposure of excess reagent to air. Ettringite was common in the acid mine drainage sludges. This mineral is often postulated to host a variety of contaminants by substitution in its crystal lattice[123], but no evidence that this phenomenon occurs has been reported for Zn (which might substitute for Ca). In any case, ettringite is unstable below the mid-alkaline pH range and releases metals through decomposition into gypsum, Al-hydroxides, and Al-hydroxy sulfates[93].

Quartz was commonly reported in the metal finishing and pyrometallurgical sludges and was also identified sporadically in some of the other sludges. It may have been carried in as particles with the wastewater during treatment, or as impurities in the lime[71]. For acid mine drainage sludge, quartz may originate from soil; in pyrometallurgical sludge, it may originate from coke, flux and ore.

Some iron oxides, oxide-hydroxides, sulfate, and hydroxyphosphates with different ratios of Fe_2O_3:P_2O_4:H_2O were also found, e.g., goethite, hematite, magnetite; akaganeite, ferrihydrite, lepidocrocite[106] ($\gamma-\mathrm{FeO(OH)}$), iron hydroxides, iron(III) sulfate[59] ($\mathrm{Fe_2(SO_4)_3}$), schwertmannite[117] ($\mathrm{Fe_8O_8(OH)_6(SO_4).nH_2O}$), which are products of waste rock and tailings oxidation and/or pyrite[71] ($\mathrm{FeS_2}$), which is a main component of the host rock. These were only found in acid mine drainage sludge; whereas ferric sulfate hydrate[57] ($\mathrm{Fe_2(SO_4)_3 \cdot 8H_2O}$), iron(II) phosphate ($\mathrm{FePO_4}$)[48], and phosphosiderite ($\mathrm{FePO_4 \cdot H_2O}$)[95] were each identified only once, in metal-finishing sludges.

Aluminium hydroxides, oxyhydroxide, phosphate, and/or sulfate were found in only a few samples, especially from aluminium anodisation, e.g., gibbsite, diaspore ($\alpha-\mathrm{AlO(OH)}$), boehmite, and basaluminite ($\mathrm{Al_4(SO_4)(OH)_{10} \cdot 4H_2O}$). Magnesium hydroxides and carbonate, such as brucite ($\mathrm{Mg(OH)_2}$) and magnesite ($\mathrm{MgCO_3}$)), were only identified once in acid mine drainage sludge[122], likely they were components of dolomitic lime used in neutralisation. Sodium sulfate[124], such as thenardite ($\mathrm{NaSO_4}$), and sodium sulfate phase III were also only identified once in the aluminium anodisation sludge.

Nacrite[95] ($Al_2Si_2O_5(OH)_4$), calcium fluoride[80] (CaF_2), and antlerite[125] ($Cu_3(OH)_4(SO_4)$ were each identified only once in metal-finishing sludge while muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$)[11], hydroxyapatite[109], and fluoroapatite ($Ca_5(PO_4)F$)[126] were each identified only once in acid mine drainage sludge.

Calcite was also reported to be a major crystalline phase in pyrometallurgical sludges, which is attributable to the use, and carbonation, of portlandite in gas scrubbing. Surprisingly, the scrubbing reaction product calcium sulfate and its hydrates were much less common compared with other sludges. Magnetite (Fe_3O_4), free iron (Fe), wustite (FeO), and hematite ($\alpha - Fe_2O_3$), were also found to be common; maghemite ($\gamma - Fe_2O_3$)[35,127] was identified only twice while periclase (MgO)[127] was found only once in this type of sludge. Steelmaking sludges were found to be enriched in iron compared to the other sludges, including other pyrometallurgical sludges.

Metals and their oxides (Zn, Cd, Ni, Pb, but not Fe), quartz (SiO_2), gypsum ($CaSO_4 \cdot 2H_2O$), and calcite were reported to be the major crystalline phases in the Zn production sludge, with magnetite identified in one sample[128]. Some metal sulfate hydrates, e.g., cobalt sulfate hydrate[25] ($CoSO_4 \cdot 4H_2O$, and $CoSO_4 \cdot H_2O$), iron sulfate hydrate (szomolnokite ($FeSO_4 \cdot H_2O$)), and lead sulfate[26,27] ($PbSO_4$), were only identified in Zn production sludge.

Table 3 Mineral phases identified in neutralisation sludges by more than one literature source*

Source	Number of samples investigated**	Calcite ($CaCO_3$)	Aragonite ($CaCO_3$)	Dolomite ($CaMg(CO_3)_2$)	Lime (CaO)	Gypsum ($CaSO_4 \cdot 2H_2O$)	Hemihydrite (Bassanite) ($2CaSO_4 \cdot 0.5H_2O$)	Anhydrite ($CaSO_4$)	Quartz/silicon dioxide (SiO_2)	Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$)	Metallic iron (Fe)	Wüstite (FeO)	Hematite ($\alpha - Fe_2O_3$)	Magnetite (Fe_3O_4)	Ferrihydrite ($Fe_2O_3 \cdot 0.5H_2O$)	Goethite ($\alpha - FeO(OH)$)	Akaganeite ($\beta - FeO(OH)$)	Magnesioferrite ($MgFe_2O_4$)	Gibbsite ($Al(OH)_3$)	Boehmite ($\gamma - (AlO(OH))$)	Aluminium phosphate ($Al_{16}P_{16}O_{64}$)	Metals & their oxides except Fe*** (Cu/Cd/Ni/Pb//Zn))	Lead sulfate ($PbSO_4$)	Barite ($BaSO_4$)
	53	Acid mine drainage neutralisation sludges																						
106 129	1	x				X																		
	1	x				X										X								
	2	X				X																		
	1					X			x															
	1	x							x				X						x	x				
	1	x				X										x								
106	4					X																		
	1					X										X								
	1					X								X		X								
108	1																		X					
	1		x											x										
130	1					X																		
109	1					X																		
	1	X				XS																		
122	1	X	X	x																				
131	4	XP														X P								
93	1	x				x	x	x		X														
	1					X	X	x		X														
	1	x				x				X														
71	2	S				XS									A									
	3	XS							S						A									S

	2	S				XS									A									S
132	1								X															
121	2					X																		
	1	X				X				x														
	1	x		x		X																		
133	1	X														X								
111	1					X				X														
126	1	X		x					X															
113	1					XS																		
114	1	x				X																		
115	1	X				X																		
59	1															X								
11	1	x				x	X																	
10	1								X S					x										
117	3													XG	G		X							
	3													XG			xG	X						
	27	Metal-finishing sludges																						
134	1							XT																
105	1	X				X			X															
47	1													X										
	1																					X		
1	1	X							X															
19	1	X				X			X															
37	1								X															
48	1								X															
60	1					X	X																	
	1	X																						
135	1	X							x				X			X						x		
61	1	x							X															
95	3	X				x			x												x			
57	1																	x						
	1	X																						
66	1								X							X								
116	1																		X	X				
15	1					X																		
68	1	X																						
136	1					X																		
80	1	X				XT			X															
124	1																		X					

125	1					X	X																	
58	1																		X					
137	1	X			x									X								XS		
	14	Pyrometallurgical sludges																						
32	1											X	X	x										
54	1	X									X	X		X										
138	1	XS									xS	XS		XS										
139	1								X				X											
	1	X									X	X												
110	1	X							X				XM	XM										
140	1					X	X																	
127	1	X									X	X		X										
8	1								X					X				X						
35	1	XS							X				XS	x										
16	1	X									X	X		X										
141	1	x									X	X		X										
28	1	X							x				X	X										
40	1	x							x		X	X		X										
	11	Zn production sludges																						
21	1				x																	X		
17	1	X				X																		
23	1								X													X		
128	1							X						X									x	
24	1	X																				X		
25	1					X																		
112	1																					X		
30	1					X	X		x													x		
26	1																					x	x	
27	1																					X	X	
33	1					X			X															

X = major phase (>10%) identified by X-ray diffraction
x = minor phase (2<x<10%) identified by X-ray diffraction
S = identified by scanning electron microscopy with energy dispersive X-ray spectroscopy
A = identified by X-ray absorption spectroscopy
M = identified by ^{57}Fe Mössbauer spectroscopy
G = identified by geochemical modelling
P = identified by X-ray photoelectron spectroscopy
T = identified by thermal analysis
* Phases identified by a single source only are discussed in the text.
** Phases summarised here may not have been identified in all samples from each reference, as these may differ in origin and characteristics; further information is available in the source.
*** Metals and their oxides include Cu, CuO, CdO, Ni, NiO, Mn_2O_3, SnO_2, Al_2O_3; Zn minerals are shown in Table 5.

6.2 Zn Speciation in Untreated Sludges

6.2.1 Zn speciation by sequential extraction

Figure 4 summarises results for sequential extraction of Zn from 17 samples reported in 8 articles, which provide an indication of the mobility of Zn in these sludges. In most cases, Zn in acid mine drainage and metal-finishing sludges was found to be concentrated in the carbonate and Fe-Mn oxides fractions, with a high potential for release if the pH shifts, especially to below neutral. Zn was less mobile, with a significant proportion bound in the residual aluminosilicate fraction, in the pyrometallurgical sludges. Gomes, et al. [93] divided the Fe-Mn oxides into amorphous and crystalline fractions, whereby Zn was found mainly in the former. One contradictory result was reported by Gao, et al. [142], who found Zn in a metal-finishing sludge to be mainly associated with the residual fraction. It should be noted that the definition of species in sequential extraction methods is strictly operational. Correlation of sequential extraction results with actual mineralogy tends to be quite poor, and, in fact, none of the reviewed studies conducted actual mineralogical analysis of phases containing Zn.

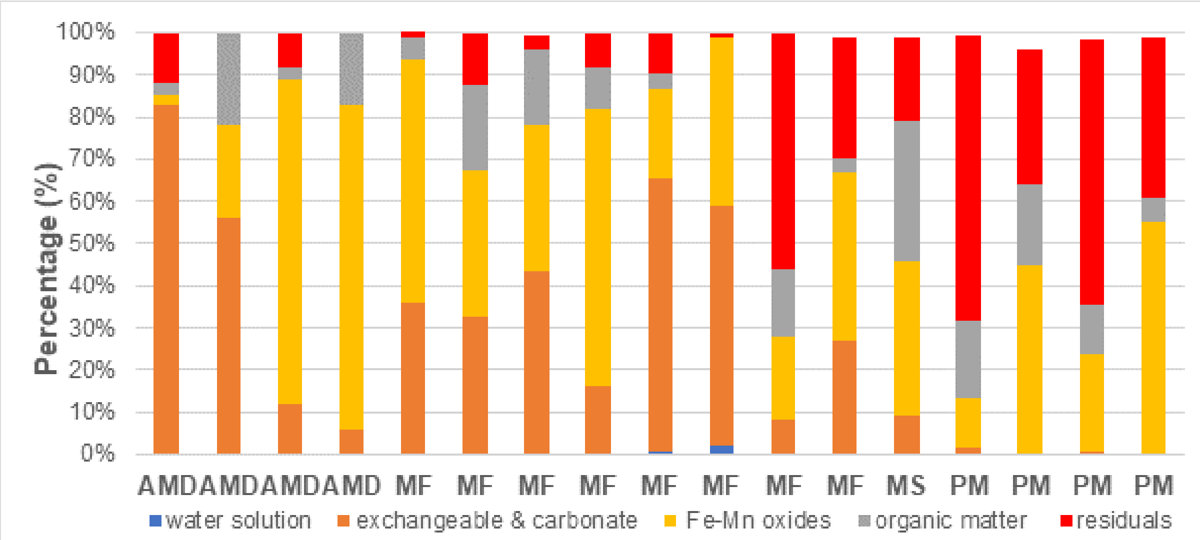

Figure 4. Operational speciation of Zn for sludges using sequential extraction. AMD: acid mine drainage sludge; MF: metal-finishing sludge; MS: metallurgical sludge from copper smelter; PM: pyrometallurgical sludge.

6.2.2 Zn speciation by other techniques

Specific, mostly crystalline, Zn species found in 12 Zn production sludges, 11 pyrometallurgical sludges, 10 metal-finishing sludges, and 8 acid mine drainage sludges are collected in Table 4

Table 4 . As was the case for the overall sludge mineralogy (6.1), most of these studies used XRD, with some results from FT-IR spectroscopy, ^{57}Fe Mössbauer spectroscopy, XPS, and XAS.

Zinc oxides and sulfates were found as major crystalline phases in both Zn production and metal-finishing sludges while metal was dominant in Zn production sludges arising from electro-winning, and hydroxides were dominant in metal-finishing sludges. Zinc sulfide was found in Zn production sludges, presumably carried over from the ore concentrate, as the hydrometallurgical processing would not result in its formation. Various zinc sulfate forms were each identified once in metal-finishing sludge, e.g. sodium zinc sulfate ($(Na_{0.8}Zn_{0.1})_2SO_4$)[66], zinc sulfate hydroxide hydrate ($Zn_x(OH)_y \bullet (SO_4) \bullet nH_2O$), ktenasite ($(ZnCu)_5(SO_4)_4\,(OH)_{12}\,(H_2O)_{12}$), and namuwite ($(Zn_{3.2}Cu_{0.8}(SO_4)\,(OH)_6 \cdot 4H_2O$)[125], while zinc sulfate and its hydrate were found in Zn production sludges. Zinc silicate, zinc phosphate[48], and zinc pyrophosphate[47] were each identified once in metal-finishing sludges. Franklinite was also identified[50,128] once in each of these sludge types. While the presence of franklinite seems implausible under the usual assumption that it originates from high temperature processes, others have suggested that it can form at ambient temperature[143,144]. On the other hand, it is uncontested that pyrometallurgical processes provide excellent conditions (e.g., steelmaking at ~1300℃) for formation of spinels such as franklinite. Indeed, spinel group and zinc carbonate minerals are the dominant crystalline phases in pyrometallurgical sludges. Zinc carbonate and its hydrates, such as smithsonite, zinc carbonate hydrate, and loseyite, were also found to be major crystalline phases in metal-finishing sludges, as well as acid mine drainage. The solubilities of $ZnCO_3$ ($10^{-9.82}$)[145] and $Zn_5(CO_3)_2(OH)_6$ ($10^{-14.9}$) [146] are much lower than that of $ZnSO_4$ ($10^{-3.01}$)[146] ; theoretically, zinc carbonate and its hydrates should therefore dominate. These findings are consistent with those from sequential extraction (6.2.1). μ-XRF and μ-XANES microspectroscopy of pyrometallurgical sludge[147] found a positive correlation between the spatial distribution of Zn and Fe, but none for the distribution of Zn and Ca. It thus seems likely that zinc carbonate phases form by atmospheric carbonation of Zn hydroxide precipitated by the neutralisation process, rather than substitution of Zn in calcite. Zinc chloride[139] ($ZnCl_2$), and calcium zincate[140]($Ca(Zn(OH)_3)_2 2H_2O$) were each identified once in pyrometallurgical sludge while zinc nitrate ($Zn(NO_3)_2$) was found once in acid mine drainage sludge[71].

Given the amorphous nature of the sludges (6.1), Zn unsurprisingly also presented in association with a variety of amorphous metal (Al, Ca, Fe, Mg, Mn, Si, and/or Zn) hydroxides, oxyhydroxides, hydroxysulfates, hydroxy phosphates, and/or silicates, identified by SEM-EDS analyses in a small subset of the sludges[60,66,71,93,95,106,109,120,129]. It should be noted that Zn may also exist in crystalline phases of low concentration, or in solid solution, also possibly at low concentration, in other minerals.

Table 4 Zinc speciation in sludges*

Source	Number of samples investigated**	Zn metal (Zn)	Zincite (ZnO)	Franklinite / Zn ferrite ($ZnFe_2O_4$)	Smithsonite ($ZnCO_3$)	Zinc carbonate hydrate ($Zn_5(CO_3)_2(OH)_6$)	Loseyite ($((Mn,Zn)_7(CO_3)_2(OH)_{10})$)	Willemite (Zn_2SiO_4)	Zinc (II) metasilicate ($ZnSiO_3$)	Wülfingite ($Zn(OH)_2$)	zinc sulfide (ZnS)	zinc sulfite and hydrates ($ZnSO_3$ / $ZnSO_3 \cdot 2.5H_2O$)	Zinc oxide sulfate hydrate ($Zn_4O_3 \cdot (SO_4) \cdot 7H_2O$)	zinc sulfate hydroxide hydrate ($Znx(OH)y \cdot (SO_4) \cdot nH_2O$)	Zinc sulfate & hydrate ($ZnSO_4$/ $ZnSO_4 \cdot H_2O$/ $ZnSO_4 \cdot 7H_2O$)	Zinc pyrophosphate/ phosphate ($Zn_2P_2O_7$/$Zn_3P_2O_8$)	zinc nitrate ($Zn(NO_3)_2$)
	8	Acid mine drainage sludge															
122	1					C	c										
131	1				F	F											
71	6																A
	9	Metal-finishing sludge															
47	1			X													
	1															X	
18	1									x				X			
37	1				XA				XA	xA							
48	1															x	
135	1		x														
57	1						x										
125	1																
137	1		xS														
	10	Pyrometallurgical sludge															
32	1			XS													
139	1								A								
	1			A		A									A		
147	1			A		A											
	1			A		A											
110	1			M													
16	1			X													
141	1		x	X													
28	1			X													
40	1		X	X													
	12	Zn production sludge															
21	1	X	x									X			X		

17	1		X					x			x	x					
23	1		X														
24	1										X						
128	1		xF	XM F				xF			x				xF		
25	1														X		
112	1	X	X														
30	1		x														
26	1	X											X	x			
27	1													X			
33	1		X												X		

X = major phase (>10%) identified by X-ray diffraction
x = minor phase (2<x<10%) identified by X-ray diffraction
S = identified by scanning electron microscopy with energy dispersive X-ray spectroscopy
A = identified by X-ray absorption spectroscopy
M = identified by ^{57}Fe Mössbauer spectroscopy
P = identified by X-ray photoelectron spectroscopy
C = identified by combined μ-XRD and μ -XRF
F = identified by Fourier transform infrared (FT-IR) spectroscopy

* Phases identified by a single source only are discussed in the text.
** Phases summarised here may not have been identified in all samples from each reference, as these may differ in origin and characteristics; further information is available in the sources.

7 Discussion

7.1 Benefits of aggregating data from disparate sources

Descriptive statistics (range, mean, and standard deviation) for the elemental composition of 161 samples from 92 papers show neutralisation sludges to be composed of at least 21 elements. Aggregation of data about useful elements (Al, Ca, Fe, Si) is relevant to the utilisation of the sludges in other industrial activities. The data for heavy metal pollutants (As, Cd, Co, Cr, Cu, Ni, Pb, Sn, Zn) can be used to assess the associated environmental risks.

Examination of the mineral phases in 120 samples from 77 papers reveals the neutralisation sludges to be complex materials composed of more than 50 phases. Nevertheless, it was possible to identify trends in mineralogical composition indicative of pollutant mobility for each of the four different sludge types, which can be useful in developing strategies for their management.

For Zn in particular, a trend approaching a straight line was observed in the log-normal probability plot of Zn concentrations for 164 samples from 91 papers. This observation suggests that, despite their disparate sources, these data can be considered to describe random samples from a larger population. The descriptive parameters (range, mean, and standard deviation) for the Zn concentrations and the identification of Zn mineral phases in 58 samples from 40 papers can help to assess the Zn recovery potential. Aspects specific to Zn recovery, sludge ultilisation, and waste treatment are discussed below.

7.2 Potential for Zn recovery from metal-bearing neutralisation sludges

The potential to recover Zn from metal-finishing sludges, which had a median Zn concentration of 3.17%, seems high. On the other hand, Zn concentrations in most acid mine drainage sludges from coal mines are probably too low for recovery. Sludges from metal mines have higher concentrations of Zn, as well as Cu, Cd, and Pb, which suggest a potential for recovery[148], but the remote geographical locations of many mines may be an additional barrier.

The common Zn recovery methods are roasting and/or leaching. The oxides, such as zincite, smithsonite, willemite, zinc metasilicate, hydrozincite, found in the metal finishing and acid mine drainage sludges are candidates for Zn recovery by low energy hydrometallurgical processing. Amorphous Zn hydroxides and oxyhydroxides can also be recovered by leaching. However, highly stable Zn-ferrite ($ZnFe_2O_4$) in pyrometallurgical sludge , which is insoluble in most acidic, alkaline and chelating media[14,32,43], is a major obstacle for the hydrometallurgical extraction and recovery of Zn. Although Zn concentrations were highest in Zn production sludges, Zn sulfide in these sludges is also problematic for hydrometallurgical recovery.

A quantitative recovery potential can be calculated for different scenarios in a region of interest, considering these barriers to recovery[149-151]. Taking the UK as an example, the Zn recovery potential can be calculated based on the median concentrations of Zn in each of the sludges (Table 2) and the quantities of all four sludges in Table 1. A total 23,000 tonnes of Zn could hypothetically be recovered each year. If acid mine drainage sludges are excluded because of low Zn concentrations, the potential is hardly affected because of the small volumes of this sludge in the UK. If pyrometallurgical sludges are also excluded, the recovery potential drops to 22,000 tonnes. If zinc production sludges are also excluded, leaving only metal-finishing sludges, the potential drops to 480 tonnes.

7.3 Utilisation potential of neutralisation sludges

Utilisation of neutralisation sludges as construction aggregates, or raw materials to produce glass, ceramics, and cement has been proposed. The sludge are rich in Al, Ca, Fe, Mg, Na, and Si (>0.5wt.%), corresponding to dominance of aluminium oxides, calcium carbonates, iron oxides, magnesium carbonate, and silicon dioxide in their mineralogies. SiO_2 is the main network-forming component of most glasses, which also needs Na_2O, Al_2O_3, CaO and MgO, etc. Ceramics usually require SiO_2 and Al_2O_3, and cements need CaO, SiO_2, Al_2O_3, and Fe_2O_3. The descriptive statistics calculated here for these elements (Table 2) can be used to evaluate the proportions and quantities of these sludges that could replace natural raw materials. For instance, to understand the amount of pyrometallurgical sludge that might replace mined sources of Fe.

The data gathered here for trace metals be used as part of an assessment of the potential for environmental pollution associated with utilisation of sludges. In the case of Zn, its high concentration and mobility may prohibit the utilisation of the sludges because the release of Zn constitutes a risk to environmental and human health. The median Zn concentration in the studied sludges is 200 times higher than that of 20 concrete blocks used as material comparators for end-of-waste assessments in the UK (median 0.009%, ranging from 0.003% to 0.026%[152]). Moreover, the oxides found in sludges have a high possibility of releasing Zn when sludges are utilised in construction materials without any further treatment. The high Zn concentration and mobility in these sludges may thus preclude utilization of these materials. As noted in relation to the Zn recovery potential, Zn in pyrometallurgical sludges is less mobile.

7.4 Prevention and treatment of hazardous metal-bearing sludges

In this paper, the generation of metal-bearing neutralisation sludges has been taken as given. They arise because liquid wastes containing toxic metals cannot be discharged to the sewer; nor is it sustainable to transport large liquid volumes for treatment. Precipitation of sludge avoids both undesirable practices. However, recovery of the metals from the sludge requires hydrometallurgical processing, i.e., re-dissolution of the metals that were precipitated. It is more efficient to recover the metals from solution, and this is indeed practiced by larger metal-finishing plants for some metals but is not economical for all metals or smaller plants. Nevertheless, development of sustainable technologies and systems to enable metal recovery directly from the liquid stream would be preferable to recovery of metals from the sludges.

Given that metal-bearing sludges are generated, recovery of metals from them reduces their hazardous character by decreasing their pollutant concentrations. Other treatment is mainly to try to reduce the mobility of toxic metals before landfilling. Stabilisation/solidification with cement is unlikely to result in any species of lower solubility than the oxides that are already the most mobile phase in these sludges. Any benefit of such treatment is limited to physical retardation of leaching. Uptake of Zn in lower mobility phases in pyrometallurgical sludges suggests that thermal treatment may be more effective. Zinc hydroxides and carbonates and their hydrates can decompose into zinc oxide below below 400℃ [153,154] and form spinel and olivine minerals at around 1000-1200℃ [64] in the presence of sufficient aluminum oxides, iron oxides, and silicon dioxide. A systematic study of the effects of thermal treatment on Zn speciation, including production of glass, cement and ceramics[44-68], is needed.

7.5 Limitations and gaps in the literature

The primary limitations of the sludge characterisation studies reviewed here are related to the techniques applied for Zn speciation. The findings from extraction methods are insufficiently specific for the fundamental mechanistic understanding of mobility, and only semi-quantitative, due to their relatively poor reproducibility[91]. Also, the dominant amorphous mineralogy could not be identified by XRD. Some techniques suitable for non-crystalline materials, such as XAS, XPS, and ^{57}Fe Mössbauer spectroscopy, which is limited to Fe-Zn bearing phases (i.e., $ZnFe_2O_4$), have not yet been widely applied in these sludges, and can also be useful for more detailed characterisation of speciation after thermal treatment.

Information about pyrometallurgical sludges was mainly limited to those from steelmaking, with only a small amount of information available for other pyrometallurgical industries, e.g., Zn or Cu. The latter may have higher Zn concentrations, which could lead to other findings. The number of Zn production sludges was also relatively low. While this study provided aggregate descriptive statistics for all elements in neutralization sludges, detailed analysis of the Zn concentration and speciation in different sludge types was conducted only for Zn. The collected sources and data could be used for more detailed investigation of other elements.

8 Conclusions

Neutralisation sludges are complex materials of low crystallinity and remarkably complex elemental and mineralogical composition. The ranges of Zn concentrations differed for the different types of sludges: acid mine drainage sludges (0.006%-22.0%), metal-finishing sludges (0.009%-43.0%), pyrometallurgical sludges (0.024%-11.5%), and Zn production sludges (1.71%-55.7%). The median Zn concentration was under 5% for all but the Zn production sludges. A free water content of 67% on average, with a mean loss on ignition of 27%, indicated a significant content of structural water and/or organic matter.

Quartz, calcite, lime, and gypsum were observed to be the dominant crystalline phases in acid mine drainage and metal-finishing sludges, followed by a group of calcium apatite, carbonate, fluoride, hydroxide, and sulfate minerals, while quartz, calcite, metallic iron, wüstite, hematite, and magnetite were found to be the dominant crystalline phases in pyrometallurgical sludges. Quartz, gypsum, and metals, such as Cd, Ni, Pb, Zn, and their oxides, were the major crystalline phases in Zn production sludges, without any observation of metallic iron.

Sequential extraction experiments suggested that Zn is primarily present in the acid-extractable and Fe-Mn oxide fractions, in acid mine drainage and metal-finishing sludges. Crystalline zinc metal, oxides, hydroxides, and sulfates, which are consistent with this fraction, were identified by XRD, also in Zn production sludges. Association of Zn with amorphous phases such as metal hydroxides, oxyhydroxides, and hydroxysulfates, which could not be characterised by XRD, was also observed. It may also exist at low concentration in other crystalline phases, including in solid solution.

Based on the identified phases, Zn in these sludges has a high potential for environmental migration, especially in an acid environment. Recovery of Zn from these sludges should be considered for resource efficiency and environmental protection. On the other hand, Zn was associated with the Fe-Mn oxide and residual fractions of pyrometallurgical sludges, whereby the latter includes the spinel group identified by XRD, which is more likely to be stable under environmental conditions.

The descriptive statistics for the body of data as a whole suggest that the sludges captured in this review are representative samples of this type of waste. Understanding of the distribution of sludge composition and Zn concentrations can support development of policy for waste management and environmental protection, and also technical development of Zn recovery, or sludge utilisation or treatment methods.

Collection of characterisation data for neutralisation sludges from 165 papers with a variety of different objectives and approaches has revealed the similarities, differences and systematic trends within this group of wastes. The approach taken in this review provides insight into the feasibility of different sludge management options. A similar approach can be taken with other waste types, for more efficient management of materials resources.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://......

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