Genesis of nonsulfide zinc deposits and their future utilization

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Abstract. Nonsulfide zinc deposits tended to be sidelined by sulfide sources in the late 19th century. The development of flotation and smelting technologies allowed the exploitation of sulfide ores and made them a useful Zn source at low costs. The commercial interest in nonsulfide zinc deposits has been renewed by the possibility of cost-efficient onsite Zn production, due to recent advances in metal extraction. The nonsulfide zinc deposits can be subdivided into 2 groups, supergene and hypogene ores. Supergene deposits develop at the expense of sulfide orebodies, in which pyrite gets oxidized and leaches the zinc from near surface environments. Zinc is dissolved and transported by groundwater, until an increase in alkalinity causes precipitation. By contrast hypogene zinc silicate (willemite) deposits originate from hydrothermal fluids of high temperature, low $\bar{f}_{O_2}$ and low HS$^-$ contents.

Introduction

Until the beginning of the twentieth century, the production of zinc metal was focused on nonsulfide ores, also called "zinc oxides" or "calamines" (Large 2001; Gilg et al. 2008). The oxidized Zn ores consist mostly of zinc silicates (hemimorphite, willemite, zinc rich clays), zinc carbonates (hydrozincite, smithsonite) and scarce zinc oxides (zincite, franklinite), hydrous zinc phosphates (tarbuttite, scholzite) and zinc-rich clays (sauconite) (Borg et al. 2003, Gilg et al. 2008). The development from Wälz kilns to differential flotation processes in the late 19th century provided the opportunity of smelting and refining sulfide concentrates, so that the major production switched from nonsulfide zinc sources to sphalerite ores (Hitzman et al. 2003; Gilg et al. 2008). In 1996, less then 5 % of the world zinc production was recovered from nonsulfide zinc ores (Gilg et al. 2008). However,
the calcination techniques and metallurgical processes, used for the recovery of zinc from sulphide ores, are very energy-intensive and the resulting sulphur compounds can pose a threat to the environment, when being exhausted to the air (Hitzman et al. 2003, Gilg et al. 2008). Nonsulfide deposits contain zinc carbonates or silicates, which can be easily dissolved in sulphuric acid, whereat gypsum is generated as a nonhazardous by-product (Gnoinski 2007). Afterwards the zinc becomes extracted to nearly pure zinc in an electrolysis process. Recent developments of cost-efficient processing by acid-leach, solvent-extraction and electrowinning thus offered a new opportunity for the commercial utilization of nonsulfide zinc ores (Hitzman et al. 2003).

**Supergene Nonsulfide Zinc Deposits**

Heyl and Bozion (1962) differentiated nonsulfide zinc deposits in two major geologic types, supergene and hypogene nonsulfide zinc deposits. This metallogenetic classification was modified by Hitzman et al. (2003). Large (2001) proposed a mineralogical categorization of nonsulfide zinc deposits: calamine (smithsonite / hemimorphite-dominant), silicate (willemite, franklinite)-dominant and hydrated zinc silicate deposits. The origin of supergene zinc deposits is related to the oxidation of sulfide and nonsulfide zinc deposits (Hitzman et al. 2003). They are the predominant type of nonsulfide zinc deposits and show widespread distribution all around the world (Fig. 1) (Holland 2005).

![FIG. 1](image)

**FIG. 1** The Location of the nonsulfide zinc deposits. Potential areas for supergene deposition are marked in the map in red. These areas show existing Zn-Pb sulfide deposits, hosted along mineral belts in carbonate rocks and a favorable climatic history (modified after Kärner 2006 and Hitzman et al. 2003).
Supergene nonsulfide zinc deposits are prevalently carbonate-hosted. Their formation is primarily controlled by climatic factors, the composition of the protore and the constitution of the wall rocks (Reichert & Borg 2008). Temperature controls the rate of oxidation and rainfall the intensity of leaching (Thornber 1992). Under humid conditions in tropical climates the groundwater is enriched in microorganisms and humic acids, but shows a depletion of inorganic anions. As a consequence favorable conditions for the mobility, dispersion and leaching of elements released from sulfides and associated gangue and wallrock minerals, are offered. Arid environments show minimal biogenic activity within the soil, so that oxygen can reach the sulfides easily and the supergene aqueous solutions show comparatively high metal concentrations (Reichert & Borg 2008). Because of the low water table in these regions, the contact between Zn-bearing fluids and the aquifer is prevented and the mobility, dispersion and dilution of metals get suppressed.

Supergene deposits can contain hemimorphite and/or smithsonite, which are products of sphalerite oxidation, and/or sauconite (Hitzman et al. 2003, Borg et al. 2003). Whether galena and chalcopyrite appeared in abundance in the precursor zinc deposit, a larger diversity of oxide, silicate and carbonate minerals occur in the supergene ores. In many cases secondary sulfides, like chalcocite, are associated with the supergene alteration of primary zinc deposits. All of the supergene deposits listed by Hitzman et al. (2003) were formed in the Cenozoic. The following subtypes are distinguished by Hitzman et al. (2003)

**Direct replacement deposits**

Direct replacement deposits can originate at the expense of Mississippi Valley-type (MVT) deposits, carbonate replacement-type "manto" deposits (Large 2001, Hitzman et al. 2003) or sedimentary-exhalative (SEDEX, SHMS) deposits (Large 2001). As a result of supergene oxidation the primary sulfide mineralization is replaced by secondary oxide, silicate and carbonate minerals (Fig. 2) (Hitzman et al. 2003). Former MVT deposits show a mineralogical simple composition and contain hemimorphite, smithsonite and hydrozincite. Carbonate replacement deposits are generated under high temperature conditions (200° - <500° C) (Megaw et al. 1988, Titley 1996). They are polymetallic with complex mineralogy (Hitzman et al. 2003). The carbonate replacement deposits show a large diversity of secondary minerals and contain smithsonite, hemimorphite, hydrozincite and prevalently manganese-rich zinc minerals such as hetaerolithe and hydrohetaerolithe, as well as copper carbonates and complex arsenic minerals.
FIG. 2 Models for the genesis of supergene nonsulfide zinc deposits (after Heyl and Bozion, 1962 and Hitzman et al., 2003) a. Direct-replacement-deposit, generated by zinc oxides and zinc carbonates by replacement of a former sulfide ore body (or zinc silicate ore body). b. Wall-rock-replacement deposit, formed by complete leaching of the sulfide ore-body, the migration into the surrounding carbonate rocks and the replacement of calcite and dolomite. c. Residual and karst-fill deposits emerge from a zinc concentration in karst cavities and sinkholes, either as a direct-replacement deposit or a wall-rock-replacement deposit.

Direct replacement deposits are formed by supergene oxidative destruction and replacement of sulfide-bearing zinc deposits in the upper, weathered parts of the former ore body. Owing to solution processes and leaching by ground water the residual zone at the top of the former sulfide deposit is depleted in Pb, Ag, Zn and S, whereas the original contents of Fe, Mg and Ca remain effectively constant throughout the zone of oxidation (Sangameshwar & Barnes 1983). Pb and Ag precipitate in the upper oxidized ore zone, Zn and S stay in solution. Iron sulfides in the primary mineralization generally possess the ability to produce sulfuric acid during the alteration process (Hitzman et al 2003). The acid results mainly from the oxidation of pyrite and/or pyrrhotite and tends to leach zinc from the near-surface environment (Large 2001). During the oxidation process H$_2$SO$_4$ gets generated. Additionally Fe$^{3+}$ serves as an oxidant to form FeSO$_4$ that reacts with sphalerite to form zinc sulfate that is soluble in acid to neutral surface waters. As a consequence Zn becomes dissolved in an aqueous solution and gets removed from the surface.

Wall-rock replacement deposits

As sulfide bodies are progressively oxidized the zinc-loaded ground water follows the ground-water gradient from the original ore body and migrates into the calcareous wall rock (Hitzman et al. 2003). When the zinc sulfate gets into contact with carbonate host rocks the basicity increases to a pH of ~8 and smithsonite replaces calcite and/or dolomite in the host rocks (Fig. 2) (Large 2001). The silicate component of the carbonate host rocks may be replaced at slightly lower pH values by precipitating hemimorphite. A Progressive variation in the redox potential during the ground water percolation leads to a zonal distribution of metal-bearing oxides and carbonates (Sangameshwar & Barnes 1983).
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FIG. 3 Generalized section through the La Calamine nonsulfide Zn-Pb deposit below recent cover as an example for direct replacement in combination with wallrock-replacement in the host carbonates (after Coppola et al. 2008)

Wall rock replacement deposits can be related to direct-replacement deposits (Fig. 3) or also to ore bodies that are completely depleted in zinc (Hitzman et al. 2003). In some cases the original sulfide body has already been removed by erosion. The intensive leaching processes are favored by high to moderate iron sulfur contents, tectonic uplift, high rock permeability and a drawdown of the water table. Different metal solubilities and processes of dissolution, transport and precipitation lead to a gradational separation of different elements and a zonal arrangement of the precipitated supergene ore minerals (Sangameshwar and Barnes 1983). Hence, the mineralogy of wall-rock replacement deposits is much simpler as in direct-replacement deposits (Hitzman et al. 2003).

The Skorpion nonsulfide zinc deposit is located in the late Proterozoic Gariep Belt in South Namibia (Borg & Kärner 2001). The ore body comprises 19.5 million tons of ore at an average zinc grade of 10.1% (www.skorpionzinc.com.na). The genesis of the deposit relies on the supergene alteration of sulfide zinc ores hosted in volcanic and sedimentary sequences (VHMS, SHMS) (Kärner & Borg 2002). The nonsulfide zinc ores consist of sauconite, smithsonite and hemimorphite (Kärner & Borg 2001) and show indications of wall rock replacement and in-situ-oxidation, respectively direct replacement (Kärner & Borg 2002). The nonsulfide zinc mineralization appears prevalently in the siliciclastic carbonate metasediments and subordinate in the metavolcanic lithologies (Kärner & Borg 2002). As the supergene minerals are undeformed, they clearly postdate metamorphism and deformation processes of the host rocks (Kärner & Borg 2002).

Residual and karst-fill deposits

The weathering of ore deposits in the proximity of carbonate rocks is accompanied by cavitation and slumping processes (Rose et al. 1979). The development of karst environments requires wet tropical climates or temperate climates with alternating wet and dry cycles and is favored by the formation of oxidizing solutions (Thornber & Taylor 1992, Hitzman et al. 2003). As a result of mechanical or chemical transport high-grade smithsonite becomes accumulated in the originated karst de-
pressions (FIG. 2) (Hitzman et al. 2003). Further leaching processes lead to the formation of hydrozincite and causes the migration into dolina and karst cavities. Mechanical concentration of smithsonite is due to sinkhole collapse, where a matrix of hydrozincite gets generated. Karst-fill deposits are relatively small in size and irregular in shape. Even so, they exhibit high grades of zinc and are attractive exploration targets for small-scale mining.

Hypogene Nonsulfide Zinc Deposits

Several carbonate-hosted zinc deposits do not appear to have formed at the expense of sulfides (Brugger et al. 2003). They are interpreted as products from saline hydrothermal fluids at temperatures of more than 100 - 150° C under oxidizing (hematite-stable) conditions with low HS⁻ contents (FIG. 4) (Brugger et al. 2003, Schneider et al. 2008). These deposits comprise mainly willemite or an assemblage of willemite, franklinite and zincite (Brugger et al. 2003). High temperatures, a low sulfur activity and a relatively high oxygen fugacity benefit the precipitation of willemite from the hydrothermal solutions instead of sphalerite and zincite occurs, if quartz is sufficiently under saturated. The formation of intergrowths of willemite with sphalerite lead to the conclusion that both formed at the same time (Hitzman et al. 2003). The deposits consist of veins and irregular pipes and their formation occurs as a result of the interaction of oxidized, silica-saturated, sulfur-poor hydrothermal fluids with carbonate host rocks (Fig. 2) (Hitzman 2001). The secondary minerals smithsonite, hemimorphite, hydrozincite and sauconite are comparatively scarce, (Holland 2005). Because of difficulties in exploration, the number of deposits is currently rather small. The most intensively studied deposits are of Mesoproterozoic to Cambrian age (Hitzman et al. 2003). Two subtypes can be subdivided.

![Fig. 4](image)

**Fig. 4** Models for the formation of hypogene nonsulfide zinc deposits. a. Formation of a hypogene structurally controlled deposit by fluid mixing between a reduced, Zn-rich, S-poor hydrothermal solution and a highly oxidized fluid along a fault zone. b. Generation of a hypogene strata-bound nonsulfide zinc deposit by mixing between a reduced Zn-rich, S-poor hydrothermal fluid and a body of oxidized, S-poor water. The sediments underneath the water body can also be affected by mixing reactions. (after Hitzman et. al 2003)
Structurally controlled hypogene deposits

Structurally-controlled willemite deposits form by structurally-controlled replacement of sphalerite ores by willemite (Fig. 4) (Hitzman et al. 2003). The deposits appear in carbonate sequences of Neoproterozoic to early Cambrian age and are locally surrounded by zones of hydrothermal dolomitization and silicification (Fig. 5).

Stratiform hypogene deposits

The stratiform subtype contains willemite, franklinite and zincite and significant amounts of manganese and iron oxides (Hitzman et al. 2003). These deposits consist of stratabound lenses of primary zinc-bearing minerals in metacarbonate calc-silicate rocks within high-grade metamorphic terrains (Fig. 4) (Frondel & Baum 1974, Hitzman 2001). Zn/Pb ratios in this deposit type are relatively high, so that their genesis is controversial (Hitzman et al. 2003). A syngenetic formation, related to a submarine accumulation of manganese and iron oxides is supposed by some authors (Degens & Ross 1969). Hitzman (2001) takes a relation to Broken Hill-type deposits in consideration. Broken Hill-type deposits have been formed from metal-rich (Zn, Pb), sulfide-poor reduced hydrothermal fluids, mixed with oxidized, sulfur-bearing fluids (Cooke et al. 2000, Hitzman et al. 2003) Hitzman et al. (2003) assume that hypogene stratiform nonsulfide zinc deposits exhibit three endmembers. The manganese end member arises from a reduced fluid, that contains Mn and Fe and subordinate base metals, mixed with an oxidized sulfide-poor fluid, the Broken Hill-type deposits in which a reduced fluid with higher base metal contents gets in contact with an oxidized, sulfur-rich fluid and the hypogene nonsulfide zinc deposits, as a combination of the other end members, emerged from reduced fluids with high base metal contents, mixed with an oxidized, sulfide-poor fluid.
Recovery of zinc from nonsulfide zinc ores

The zinc production still concentrates predominantly on the mining of zinc sulfide ores, because the separation from the gangue works comparatively easy and the zinc concentration is based on conventional flotation techniques (Hosseini 2008). By contrast the recovery of zinc by conventional flotation of oxide zinc ores is not high enough. Flotation of the zinc oxide minerals smithsonite, hemo- morphite and willemite with conventional collectors is not very selective (Bustamante & Shergold 1983). Reasons for the poor selectivity include similarities in the surface chemistry of the zinc and gangue minerals. However, in consequence of new developments in hydrometallurgy the economic interests in nonsulfide zinc deposits increase (Hitzman et al. 2003). The recent development of hydrometallurgical acid-leaching, solvent extraction (SX) and electrowinning (EW) technology converted them to attractive exploration targets with the capability of becoming a major source of zinc for the twenty-first century (Large 2001, Cole & Sole 2002). Due to the fact that they don’t contain sulfur nonsulfide zinc deposits offer a big advantage for the environment, because there is no disposal of sulfur and sulfuric acid required (ZincOx Annual Report 2007). Zinc from nonsulfide minerals can be recovered as metal or as an industrial grade zinc oxide by dissolution from the ore directly without prior concentration. In this way the maximum value of the zinc is obtained and sharing the value of the metal with a third party smelter is avoidable.

The solvent extraction/electrowinning (SX/EW) process

The Skorpion Zinc Project uses the leach/solvent extraction/electrowinning/leached to metal process and demonstrates the viability of the production of zinc from nonsulfide zinc ores (de Wet & Singleton 2008). The recovery is based on direct leaching in dilute sulfuric acid to produce zinc sulfate (skorpionzinc.com.na, ZincOx Annual Report 2004). Direct electrowinning technologies are not operational because of the high amounts of impurities, like chlorine and fluorine, in the ore (http://www.skorpionzinc.com.na). Anode and cathode corrosion and cathode stripping problems would be the result. The use of solvent extraction for zinc provides a buffer against fluorine and chlorine and prevents any carry-over into the electrolyte solution. The electrowinning process uses electrical power for the metallization of zinc on solid cathodes out of a loaded electrolyte solution. The zinc sulfate solution is contacted with an organic matter to extract zinc as an organic complex. Spent electrolyte becomes sent back to the loaded organic matter in order to produce a zinc containing electrolyte (loaded electrolyte). In the electrowinning cellhouse zinc cathode sheets (SHG) with a zinc content of 99.995 % are produced from the loaded electrolyte and do not require further refining. The remaining spent electrolyte gets reinserted into the loaded organic matter. Finally zinc products are produced by melting and casting.
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The Leach to chemical (LTC) process

A common problem in nonsulfide zinc deposits is the high alkalinity of the carbonate host rocks (ZincOx Annual Report 2004). The high amounts of carbonates need to be dissolved by sulfuric acid. The acid used for the dissolution of zinc with the solvent extraction/electrowinning/leached to metal technology is quickly neutralized and the costs of consumed acid is able to prevent the economic development of a deposit. Lower amounts of carbonate minerals lead to a decline of the high acid consumption and can be achieved by concentration of the zinc bearing ore minerals. The ore concentration is achieved by separation, floatation and fuming. But because of poor separation and low recovery ZincOx started to use the hydrometallurgical LTC (Leach to chemical) process at their deposit in Jabali, Yemen in 2005. This technology is opposed to the LTM (Leach to metal) procedure at the Skorpion mine and produces high purity zinc oxide, rather than zinc metal. In this process no acid is in use and the reagents can be recycled. The process involves crushing of the ore, calcination, leaching and purification and produces a high quality zinc oxide. (http://www.ansanwikfs.com) The zinc oxide (ZnO) is produced by burning zinc fumes with air (http://www.zincox.com). Zinc salts, zinc carbonate or zinc hydroxide are calcined (heated) to obtain zinc oxide. Afterwards secondary materials such as zinc sulphate solution, or oxidised ore get dissolved in appropriate leaching liquor. The produced zinc oxide is of sufficient quality for sale to industrial consumers and commonly leads to an increase in the metal content of between 5% and 15% (Zinc Ox Annual Report 2004). The use of the LTC technology leads to enhanced revenue and lower operating costs, because the energy consumption is lower in comparison to the electrowinning technology.

FIG. 6   Zinc recovery from zinc oxide ore at the Skorpion Zinc mine in Rosh Pinah, Namibia Aqueous leaching: ore is leached with aqueous raffinate to produce zinc sulfate organic extraction: consists of a mixture of the extractant Di-2-Ethyl-Phosphoric Acid (D2EHPA) in diluent (kerosene) (www.skorpionzinc.com.na)

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Projects under development

The Solvent extraction process for primary ore is intended to be used in different non-sulphide ore projects (Cole & Sole 2002). Recent examples of developed projects that use the zinc solvent extraction for zinc oxides, silicates and carbonates are the Shaimerden deposit in Kazakhstan, the Angouran deposit in Iran, the Sierra Mojada deposit in Mexico and the Accha deposit in Peru. BHP Billiton developed a process for the recovery of zinc from geothermal brines. This process is currently used by the company Kvaerner Metals at a project of CalEnergy Minerals in the Imperial Valley of California for power generation from a high-temperature underground brine, in which Zinc is bond in anionic complexes. The hot brine passes through an ion-exchange column, where zinc is adsorbed before the brine is pumped back into the underground. Other elements remain dissolved as cations in the brine. A concentrated zinc solution is produced by reverse osmosis and becomes purified by solvent extraction, before zinc cathode is produced by the electrowinning process. The operation is expected to recover 30 000 t/a zinc and is one of the cleanest zinc-recovery operations ever undertaken. The solvent extraction process is also utilized as a part of the recycling process for purification and upgrading of secondary zinc-bearing materials. Further fields of application of the solvent extraction process are the zinc recovery from spent batteries, the reprocessing of furnace dusts, zinc tankhouse bleeds and process residues and tailings.

Discussion

By using the solvent extraction circuit high zinc recoveries can be reached by little environmental hazard (Cole & Sole 2002). However, gypsum precipitates in large amounts during the process by leaching of zinc oxide with sulfuric acid. These huge amounts still remain a problem. By using a source of pure lime, "white gypsum" can be produced. This product can be used in the plasterboard industry. Another problem is the lack of high by-product profits at nonsulfide zinc deposits that sulfide deposits typically make from Pb and Ag (Hitzman et al. 2003). Both, the application of the solvent extraction technology and the amount of non-sulphide zinc ore projects are expected to increase in the near future. The increase of economic significance relies on the low processing costs for the on-site production of zinc metal, compared to the zinc production from sulfides and on the lower degree of environmental pollution (Large 2001; Gilg et al. 2008 a). Furthermore the high reactivity of various wall rocks causes a high concentration of zinc and makes them economical attractive (Hitzman et al. 2003). It is assumed that the appearance of sulphide zinc deposits in proximity to reactive carbonate trap rocks may be useful targets for further exploration for non-sulphide zinc deposits. Future deposits need to be large and high grade (>12 % Zn) to be economically viable and must have potential for multiyear production to offset the high costs for a hydrometallurgical plant.
References


