# Two-Step Neutralization Ferrite-Formation Process for Sustainable Treatment of Acid Mine Drainage from Abandoned or Closed Mines

（休廃止鉱山からの酸性坑廃水の持続可能な処理法としての

二段中和フェライト生成プロセス）

## 学位論文内容の要旨

Acid mine drainage (AMD) is the most widespread and serious environmental pollution problem facing the mining industry. AMD flowing into water bodies can have devastating effects on these habitats. Generally, water streams receiving AMD become unfit for desired uses. Impacted uses include agricultural, industrial, recreational, scenic view, and human consumption. Operating mines are bound to treat the AMD generated in the mine sites before discharging it. However, since many closed and longtime abandoned mines lack economical resources or have no legal owners, local or national governments have to undertake the AMD treatment. In Japan by the year 2000 there were 5,487 abandoned or closed mine sites countrywide. Many of these abandoned or closed mines have been generating AMD for several decades. The most often adopted AMD treatment technology is a conventional AMD neutralization in which a chemical (lime, limestone, hydrated lime, or NaOH) is added to the AMD to neutralize acidity and precipitate heavy metals. Currently, sludge disposal is becoming an important environmental problem because of the risk of toxic elements re-release. Thus, there is a strong need for a technology that confers sustainability to AMD treatment. Therefore, the main objective of the present research is to develop an AMD treatment process that can confer long-term sustainability to the treatment of AMD from abandoned or closed mines. The current research proposes a "two-step neutralization ferrite-formation process" as the most suitable alternative for dealing with the AMD environmental problem in a sustainable fashion.

Chapter 1 gives an introduction on the AMD issue (generation of AMD, its consequences, and the available options for its control and treatment), the objectives of the research, and the synopsis of the dissertation.

Chapter 2 gives an overview of previous works on ferrite formation processes, a description of the new process proposed, and the experimental procedures. The two-step neutralization ferrite-formation process developed in this research has two neutralization steps and uses two different neutralizers in order to control the solution chemistry. The treatment plant consists of one retention tank, two continuously stirred tanks (one for each neutralization step), and two sedimentation tanks for solid-liquid separation. The AMD is continuously pumped into the first neutralization tank, where 1.5 wt% MgO slurry is added (first neutralization step) to precipitate metal hydroxides of low solubility at a pH of about 4.8. The precipitate (first sludge) is separated from the partially neutralized AMD in the first sedimentation tank. The partially neutralized AMD flows to the second neutralization tank (ferrite formation tank), where 1N NaOH solution is added to precipitate the remaining dissolved metals together with ferrous and ferric hydroxides at a pH of 8.5. The first neutralization step using MgO was designed to avoid the influence of some AMD constituents that are detrimental to ferrite formation, e.g., Al and Ca, NaOH was selected as the second neutralizer because it favors ferrite formation when detrimental AMD constituents are present in the solution.

In Chapter 3 the results and discussion of batch experiments are given. Batch tests were performed to determine the Al removal efficiency of MgO, to determine the neutralizer consumption, and to compare

the behavior of AMD constituents when neutralized by $CaCO_3$ (commonly used in AMD treatment) or MgO (neutralizer in our process). For this 100 mL of AMD was placed in a 200 mL beaker and neutralized to a pre-determined pH. The resulting suspension was filtered for dissolved constituents analysis. These tests showed that MgO had a better neutralizing capacity (about twice per unit weight) than $CaCO_3$. The precipitation of Al depended greatly on pH rather than on the type of neutralizing agent. Therefore, the elimination of Al in the process can be controlled by the dosage of neutralizer. For different simulated and actual AMDs, Al started to precipitate massively at about pH 4.0 and was completed at about pH 5.2 irrespective of neutralizing agent, MgO or $CaCO_3$. Ferrous iron started to precipitate massively at about pH 6.0 or above. This pH difference (1 to 1.5 pH units) between the end of massive precipitation of Al and the beginning of $Fe^{2+}$ massive precipitation gives a good window to effectively separate Al from $Fe^{2+}$. The elimination of Si was more difficult than the removal of Al, and its elimination was independent of the precipitation of Al, rather it seemed related to the precipitation of Fe. For simulated AMDs the removal of Si was favored by MgO addition, but for the actual AMD this was not so evident. The batch tests with actual AMD showed that Al, Cu, As, and $Fe^{3+}$ were removed simultaneously and selectively from $Fe^{2+}$.

Chapter 4 presents the results and discussion of continuous flow tests. In this case a few hundred litters of AMD were treated in each run as described in Chapter 2. Dissolved constituents were monitored at the inflow, in the two neutralization tanks, and the treated water. The continuous flow tests showed that the first neutralization pH was an important variable to control the removal of Al and Si as well as the plant setup adopted for the treatment. Adopting a setup with the first sludge separation tank favored the purposes of the proposed process. The fraction of initial $Fe^{2+}$ removed in the first neutralization step was inverse to the initial iron concentration at the inflow. Thus, the two-step neutralization ferrite-formation process may not be suitable for treating AMDs with low ferrous iron content because a big portion of the iron would be lost as first sludge leaving the second step unable to form ferrites. The consumption of neutralizer was higher than the optimum calculated and was more pronounced when $CaCO_3$ was used instead of MgO. This higher neutralizer consumption may be due to their slow dissolution. During the first neutralization MgO had much better removal of Al, Si, Cu, Zn, and As than $CaCO_3$. Therefore, MgO yielded a partially neutralized AMD with better chemical composition for generating second sludge containing ferrites.

In chapter 5, the characteristics of the sludge and treated water are given. The sludges were analyzed by XRF, XRD, and XANES to determine the chemical composition, mineralogical phases, and the oxidation state of As. The sludges were subjected to settling, dewatering, and leaching tests to determine their physical characteristics and chemical stability. The chemical composition of the sludge (first and ferrite) depended on the characteristics of the inflowing AMD, the pH at which the first neutralization was performed and the proper dosage of neutralizer. At high Al concentrations in the raw AMD, Al species predominated whereas at low Al contents, Fe species were predominant. Another important constituent of the first sludge was the non-dissolved neutralizer (generally around 10%, but in some cases up to 26%). Iron species dominated the composition of ferrite sludges and their proportion increased with higher pHs at the first neutralization. The main mineralogical phases detected in the first sludge from simulated AMD depended on the neutralization pH. For pH of 4.3 the first sludge was mainly amorphous whereas at pH 4.6 it was slightly more crystalline (presence of gibbsite and some periclase). The ferritization of the ferrite sludge was greatly influenced by the Al/Fe and Si/Fe molar ratios. Thus for a simulated AMD with medium-low Fe and high Al content, amorphous iron hydroxide dominated. In a case with high Fe, low Si and medium Al concentrations, well-crystallized ferrites (magnetite and magnesioferrite) were almost the only constituents, whereas the sludges from similar cases but with higher Si content had very low ferrites content. However, low Al/Fe and Si/Fe ratios were not enough to reach complete ferritization of the sludges. The total amount of iron was also an important factor to reach complete ferritization. The magnetic characteristics of the sludge depended on the mineralogical composition of the sludge: Higher ferrites content gave the sludges higher saturation magnetization. However, when other ferrites than magnetite were present the saturation magnetization decreased considerably. Sludges with higher ferrites content settled faster during solid-liquid separation. Higher suspended solids in the ferrite formation tank yielded sludges with lower SVI and better dewaterability characteristics. The first and ferrite sludges from the actual AMD treatment showed good stability with respect to As, Cu, and Zn leachability. Arsenic in the first sludge was present as As(III) and As(V), As(V) being in higher proportion than As(III). The fraction of toxic metals leached from the sludges represented only about 0.002% of the amount held in the first sludge generated by using MgO and about 0.2% of the amount held in the ferrite sludge. The treatment of simulated and actual AMDs by the two-step neutralization ferrite-formation process showed that this

process is effective in improving the water quality to environmental acceptable levels. The process delivered treated water with parameters such as pH, Fe, Al, Cu, Zn, and As that were always within the range of the water discharge standards, and in many cases within the drinking water standards. In Chapter 6 the most important general conclusions of this research are summarized.

# 学位論文審査の要旨

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　酸性坑廃水 (AMD) に対する処理対策は, 鉱業分野における最も重要な環境問題の一つである。それは坑廃水処理が操業中だけでなく閉山後にも及ぶからである。日本では 5,500 程度の休廃止鉱山が存在し, 主要な坑廃水は処理されている。従来の処理法では, 炭酸カルシウムや水酸化カルシウムを中和剤として酸性坑廃水を中和し, 含有重金属類を沈殿除去している。しかし, 生成する中和殿物は膨大となりその埋立に多額の費用を要するとともに, 重金属類の再溶出も危惧される。したがって, 坑廃水処理を持続可能な技術とすることが必要となってきている。本研究では, 持続可能な坑廃水処理技術として二段中和フェライト処理法を提案するものである。

　第 1 章では坑廃水の生成, 環境への影響, これまでの処理法を紹介するとともに, 本研究の目的と論文の構成を記述している。

　第 2 章では従来のフェライト処理をレビューし, 新たなフェライト処理法とその手順を記述している。本研究で提案する二段中和フェライト処理法は, 酸化マグネシウムあるいは炭酸カルシウムを第一段目の中和剤, 水酸化ナトリウムを第二段目の中和剤として用いる二段中和プロセスで, 2 個の攪拌中和槽と 2 個の沈殿槽から構成されている。第一段目の中和では pH を 4.8 程度に上昇させ, 第二鉄イオン, アルミニウム, ヒ素などを除去し, 第一段目の沈殿槽でそれらの殿物を除去する。第二段目の中和では pH をさらに 8.5 まで上昇させ, 残留した第一鉄イオンなどを中和し, 鉄を主体とする殿物を生成し, 第一鉄と第二鉄からフェライト (マグネタイト) を生成する。第二段目の沈殿槽ではフェライト殿物と上澄水とを分離する。したがって, 第一段目の沈殿槽は後段のフェライト生成を阻害するアルミニウムなどを除去する役割を有する。

　第 3 章ではバッチ中和試験について記述している。バッチ試験では, 第一段目の中和処理における中和剤の種類による各種元素の除去特性の相違や中和剤消費量を明らかにした。その結果, 第

一段目の中和剤として酸化マグネシウムは炭酸カルシウムの約半分の添加量で効率的に中和できること, フェライト阻害元素であるアルミニウムの除去は中和剤の種類によらず pH に依存することがわかった。すなわち, 坑廃水の種類にかかわらず, アルミニウムは pH4 程度から沈殿を開始し, pH5.2 でほぼ完全に沈殿除去できた。また, 第一鉄イオンは pH6 以上で沈殿することから, アルミニウムと比較すると沈殿する pH に 1〜1.5 の差異があることがわかった。このことは, アルミニウムと第一鉄イオンとを効果的に分離できることを示す。一方, ケイ酸に対しては, 特定の pH 付近で除去できず, pH の増加とともに徐々に液相から除去されることがわかった。第二鉄イオン, 銅, ヒ素に対しては, アルミニウム同様, 第一段目の中和で沈殿除去できた。

第 4 章では連続通水試験について記述している。連続試験の処理水量は 1 日 36L とした。本装置を用いて第一段目の中和は pH4.3〜4.8, 第二段目の中和は pH8.5 として連続試験を実施し, 流入水, 中和槽, 流出水の水質を測定した。その結果, 流入水の水質の第一鉄イオン濃度が高く, ケイ酸濃度が低い場合は, 第二段目の中和殿物のフェライト化は効率的に達成された。また, 炭酸カルシウムよりも酸化マグネシウムのほうが第一段目の沈殿槽で効果的にアルミニウム, ケイ酸, 銅, 亜鉛, ヒ素を除去できた。このことは, 酸化マグネシウムのほうがフェライト処理には有利であることを示す。

第 5 章ではフェライト処理によって生成した殿物の性状を蛍光 X 線分析, X 線回折分析, 磁化測定などによって明らかにした。第一鉄濃度 800 mg/L, ケイ素濃度 5 mg/L を含有する模擬坑廃水から生成された殿物からは非常に純度の高いフェライトが得られた。しかし, ケイ酸およびアルミニウムの濃度の増加とともに, 第一鉄イオン濃度の減少とともにフェライト含有率が低下した。また, 殿物がフェライト化することによって, 殿物の沈降性, 脱水性が向上すること, ヒ素などの有害重金属類の再溶出も小さいことが明らかになった。これらのことから, 性状として第一鉄イオン濃度が高く, ケイ酸濃度が低い坑廃水がフェライト化に適しており, 第一段目の中和を未溶解分の少ない酸化マグネシウムを使用し, pH5 付近に調整することによって共存アルミニウムなどを除去することがフェライト化に有利であることがわかった。

第 6 章では本論文の結論を記述した。

これを要するに, 著者は, 坑廃水処理にともない発生する中和殿物から再利用可能なフェライト (マグネタイト) を生成する坑廃水条件および処理フローを提案するとともに, 坑廃水処理から生成されたフェライトの性状を明らかにしている。これは, 休廃止鉱山坑廃水の処理技術に関する新たな知見であり, 資源システム工学, リサイクル工学に貢献するところ大なるものがある。

よって, 著者は, 北海道大学博士 (工学) の学位を授与される資格あるものと認める。