



Energeia

Thermochemical Process for Utilization of Gypsum and Pyrite Wastes

Daniel Tao, B.K. Parekh, University of Kentucky
Malcolm Hepworth, University of Minnesota

Pre-combustion coal cleaning and post-combustion flue gas desulfurization (FGD) using lime or limestone are the primary processes employed to reduce sulfur dioxide (SO_2) emission from coal combustion. However, these processes generate voluminous solid wastes, i.e., pyrite and gypsum, that are usually landfilled, occupying thousands of acres of land and creating serious land and water pollution problems due to the release of acids and toxic substances. A thermochemical process has been developed for the combined utilization of gypsum and pyrite wastes by converting them into useful products such as lime, sulfur, and iron, as shown in Figure 1.

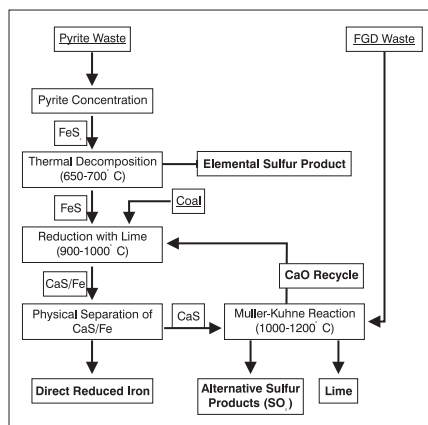


Figure 1. Thermochemical process for utilization of pyrite and gypsum wastes.

The process primarily consists of four steps:

1. Pyrite (FeS_2) is concentrated from tailings discharged from coal-cleaning

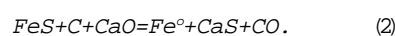
operations. This is achieved by physical separation processes such as gravity separation and flotation. These processes are based on the difference of pyrite and other tailing components in the specific gravity, surface hydrophobicity, surface charge, and interactions with the chemical reagents added. The Falcon Concentrator is one of the most effective techniques for pyrite separation from coal.

2. Pyrite is thermally decomposed to pyrrhotite (FeS) and elemental sulfur:



This reaction requires a non-oxidizing atmosphere and a temperature of 650–700° C for favorable kinetics. The labile sulfur vapor from the decomposition of pyrite is removed by condensation. The composition of pyrrhotite produced depends on the reaction temperature, retention time, and particle size of pyrite. Results have shown that pyrite is readily decomposed above 650° C under nonoxidizing conditions, producing the pyrrhotite with an S/Fe ratio of slightly larger than 1. Approximately 42% of sulfur can be removed from pyrite by thermal decomposition. Impurities such as arsenic, lead, and selenium in pyrite evaporate and report with elemental sulfur during this process.

3. Pyrrhotite is reacted with lime in a reducing environment to form calcium sulfide and direct reduced iron (DRI):



Improving the Utility of ICPMS

Kathryn L. Ackley
Graduate Student,
University of Cincinnati

INTRODUCTION

Inductively coupled plasma mass spectrometry (ICPMS) is one of the most widely used techniques for the routine determination of trace elements in aqueous solutions. Most metals and metalloids can be detected with ICPMS. The detection limits for most metallic species are in the ng ml^{-1} to pg ml^{-1} range. The detection limits for metalloid species are slightly higher in the ng ml^{-1} to $\mu\text{g ml}^{-1}$ range. ICPMS provides excellent sensitivity, a large linear dynamic range, and is capable of performing multi element analyses. These features have propelled ICPMS to the forefront of trace and ultra trace elemental analysis.

ICPMS is frequently used as a detector for elemental speciation studies. Elemental speciation refers to the separation and quantification of different chemical forms of an element. Elemental speciation is important because the toxicity or bioavailability of an element may be highly dependent upon its chemical form. For example, chromium (III) is essential for proper health in humans; although chromium (VI) is toxic and carcinogenic. Inorganic forms of arsenic are toxic, but methylated forms of arsenic are less toxic. Arsenic compounds such as arsenobetaine are nontoxic. ICPMS is a sensitive, element specific detector that can be coupled with chromatographic techniques to perform elemental speciation.

Despite its advantages, ICPMS still suffers from several significant limitations that prevent it from emerging as

Thermochemical Process, continued

Steps 2 and 3 can be accomplished as a two-stage fluidized-bed process with reaction (1) as the first stage and reaction (2) as the second stage. The hot off-gas, rich in CO from the second stage would provide the enthalpy for the first stage of reactions.

Figure 2 shows the thermogravimetric analysis (TGA) data on effects of temperature on the kinetics of reaction (2). A strong dependence of the

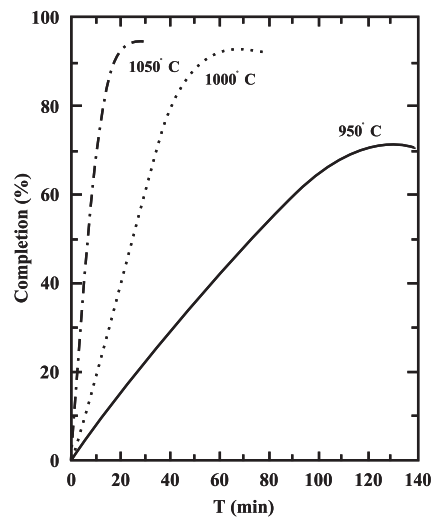


Figure 2. Rate of pyrrhotite reduction with carbon and lime as a function of temperature

reaction rate (k) on temperature (T) is observed. At 950° C the reaction reaches only 70% completion in more than two hours, while at 1050° C 95% completion is reached in 30 minutes. The rate constant of the reaction can be estimated from the slope of the linear part of the curve shown in Figure 2 and correlated with the temperature T in Equation (3):

$$\ln k = -35.955 \times 10^3 / T + 28.96. \quad (3)$$

The activation energy is determined to be approximately 299 kJ/mol, which is in excellent agreement with the result of 308 kJ/mol published by others. Figure 3 shows the X-ray diffraction (XRD)

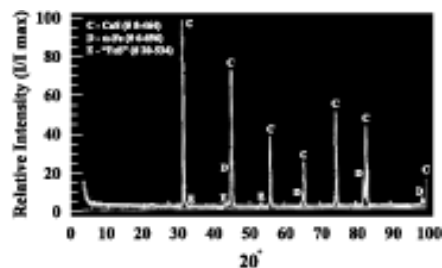


Figure 3. XRD (Cu $K\alpha 1$ radiation, $\eta = 0.15406$ nm) pattern of reaction products.

pattern of the reaction product obtained after reaction at 1000° C for 65 minutes. The pattern consists of strong intensity peaks corresponding to calcium sulfide (C) and α -iron (D) and weak peaks of unreacted pyrrhotite (E).

Figure 4 shows the effect of surface area on the rate of reaction of mixtures with different FeS:CaO:C mole ratios at 1000° C. The lime content in the initial

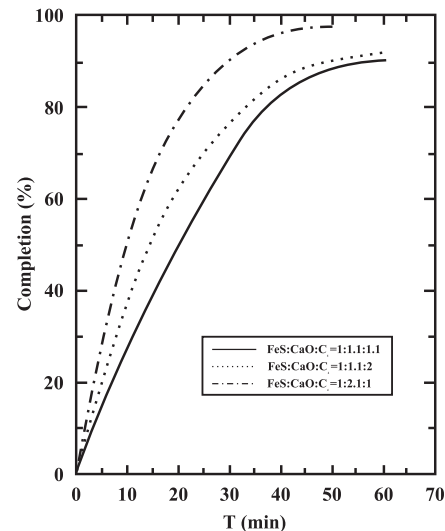


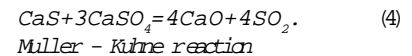
Figure 4. Rate of pyrrhotite reduction as a function of the initial lime and carbon contents at 1000° C

mixture has more significant effects on the rate of the reaction than carbon content. The 50% completion time is decreased from 20 minutes to 15 and 10 minutes by doubling the initial carbon content and lime content, respectively. Increase in lime content also reduces sulfur content in iron. This is because the desulfurization of iron with lime is controlled by the solid state counter-diffusion of oxygen and sulfur through calcium sulfide, which builds up and surrounds lime. By increasing the lime content in the initial mixture, the lime surface area is increased. Therefore thinner calcium sulfide layers are produced during the reaction and less time is necessary for oxygen and sulfur to diffuse through these layers. The XRD analysis shows that the excess calcium oxide does not react with iron and remains in the mixture as a pure phase.

The effective separation of the iron product produced in reaction (2) is necessary for the process to proceed. Magnetic separation is one of the techniques that can be used to separate iron from calcium sulfide due to their difference in magnetic susceptibility. The composition of the separation product depends on the reaction temp-

erature. With the reaction product obtained at 1000° C, magnetic separation produced the magnetic product that recovered 97.5% iron and rejected 86.7% calcium and 88.7% sulfur.

4. Calcium sulfide is employed as a reductant to react with gypsum wastes to produce lime and sulfur dioxide:



The kinetics of the Miller Kuhne reaction has been studied as a function of temperature. The results shown in Figure 5 indicate that at 1150° C 90% completion is reached in about 20 minutes and slower reaction kinetics is observed at lower temperatures. The reaction rate and the completion extent

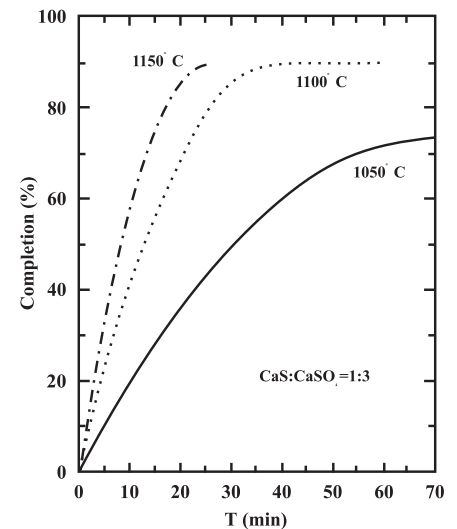


Figure 5. Rate of the reaction between calcium sulfide and FGD waste as a function of temperature

are only slightly decreased in the presence of CaO. The XRD analysis has shown that the product mixture consists of CaO and traces of CaSO_4 and CaS. It should be noted that complete conversion of gypsum is not necessary in this process since recovered lime does not require a high purity for recycling to flue gas scrubber. The rate constant k for reaction (4) can be described in Equation (5):

$$\ln k = -35.955 \times 10^3 / T + 28.96. \quad (5)$$

which results in an activation energy of 239 kJ/mol.

Figure 6 shows the effect of surface area or relative abundance of CaS and CaSO_4 on the reaction rate at 1050° C. The stoichiometric mixture (with $\text{CaS}:\text{CaSO}_4 = 1:3$ mole ratio) reaches 73% of reaction

(continued, page 3)

completion within an hour. The mixture with a 3 time stoichiometric excess of CaS (with CaS:CaSO₄ =1:1 mole ratio) yields 82% completion at 60 minutes and the mixture with a 2 time stoichiometric excess of CaSO₄ (with CaS:CaSO₄ =1:6 mole ratio) reaches 96% completion at the same time. The

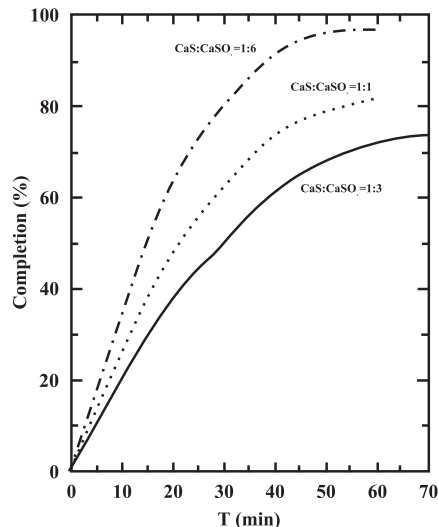
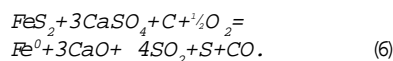


Figure 6. Rate of reaction between calcium sulfide and calcium sulfate as a function of the initial reactant concentration at 1050° C

results indicate that the excess of the reactants, particularly CaSO₄, enhances the degree of reaction completion, which represents a favorable economic situation for the recovery of lime through the Muller-Kuhne reaction.

In conclusion, pyrite and gypsum wastes can be utilized by converting them into iron, lime, and sulfur products using a thermochemical process. The overall reaction can be represented by:



The reduction of pyrrhotite with carbon in the presence of lime has a favorable kinetics above 950° C. A stoichiometric excess of lime and carbon in initial mixtures enhances the rate of the iron production and increases the degree of reaction completion. Magnetic separation can be used to separate iron and calcium sulfide, producing a magnetic product that recovers 97.5% iron and only 13.3% calcium and 11.3% sulfur. The Muller-Kuhne process is effective in converting gypsum to lime that can be recycled to FGD processes.

Dr. Tao may be contacted at:
tao@caer.uky.edu



THE SOUTH AFRICAN COAL
ASH ASSOCIATION (SACAA)

An Overview

Guides on the use of South African fly ash as a cement extender

The SACAA is producing a series of guides on the use of South African fly ash as a cement extender and the influence it has on the properties of cement-based products, mainly concrete, but also on mortars and plasters.

For more information, contact:

Marybeth McAlister:
telephone (606) 257-0224

or

President, SACAA:
P.O. Box 3017
Randburg, South Africa
email: richonne@cis.co.za

ICPMS, continued

the process for trace elemental analysis. A few of the chief limitations are listed here

1. The instruments are designed for liquid sample introduction. Modifications to the sample introduction system must be made for the introduction of gaseous or solid samples.

2. Aqueous samples with high amounts of dissolved solids (>2%) can not be analyzed since blockages may form on the sampler and skimmer cones

or in the nebulizer.

3. Conventional sample introduction suffers from low sample transport efficiency since only about 2% of the liquid sample entering the sample introduction system actually reaches the plasma.

4. Interferences. Spectroscopic interferences occur when another species has the same mass to charge ratio as the analyte of interest. These interfering species may be polyatomic ions which form from elements in the plasma gas, entrained atmospheric gases, or the sample matrix. The interfering species may also be another stable, naturally occurring isotope of another element. Non-spectroscopic interferences may enhance or suppress the analytical signal. These interferences are a result of factors which influence the aerosol transport efficiency, atomization and ionization of the analyte, or the extraction of ions from the plasma. Non-spectroscopic interferences are sometimes referred to as "matrix effects."

A variety of techniques exists which expand the utility of ICPMS by minimizing interferences, increasing sample transport efficiency, and allowing a wider range of sample types to be analyzed. Some of these techniques have been practiced for several years while others are relatively new to the field, but they all offer solutions to difficult analytical problems.

LIQUID SAMPLE ANALYSIS

Liquid sample introduction in ICPMS is notorious for low sample transport efficiency. Liquid samples are typically introduced to the instrument at a rate of 1 ml min⁻¹. Introducing samples at significantly lower flows with a conventional nebulizer results in a corresponding decrease in analytical signal. Frequently, analysts may be given samples that are only a few milliliters in volume. These volumes may not be sufficient to complete a multi-element analysis with ICPMS. To alleviate this problem low flow nebulizers such as the microconcentric nebulizer (MCN), direct injection nebulizer (DIN), high efficiency nebulizer (HEN), and the oscillating capillary nebulizer (OCN) have been developed. Low flow nebulizers provide higher sample transport efficiency and allow samples to be introduced to the instrument at low flow rates. These nebulizers help conserve small samples and also allow low flow chromatographic techniques

(continued, page 4)

ICPMS, continued

such as capillary electrophoresis and microbore high performance liquid chromatography to be coupled to ICPMS.

Therospray nebulization is a technique that achieves higher sample transport efficiency by forming an aerosol that has smaller droplets than those typically produced by standard pneumatic nebulization. The liquid sample is forced through a heated capillary where partial vaporization of the sample takes place. When the heated sample and nebulizer gas exit the capillary, a fine aerosol is formed. Lower detection limits have been reported with therospray nebulization than with pneumatic nebulization. Vanhoe et al. found the detection limits obtained with therospray nebulization for the 9 elements studied to be lower on average by a factor of 10 than those obtained with pneumatic nebulization.

Hydride generation is a technique that improves sensitivity as well as reduces non-spectroscopic interferences. Liquid samples are subjected to chemical pretreatment usually with sodium tetrahydroborate (III) to convert the analyte of interest into a volatile hydride. Hydride generation allows the analyte to be introduced to the plasma in gaseous form improving sample transport efficiency. Ionization is also enhanced since energy from the plasma is not used for desolvation and vaporization. This is a selective technique since only arsenic, tin, lead, antimony, bismuth, germanium, selenium, and tellurium are capable of forming gaseous hydrides at room temperature. As a result, the analytes are removed from the sample matrix reducing non-spectroscopic interferences. This technique is particularly helpful when coupling liquid chromatography with ICPMS for the separation and detection of hydride forming species.

Flow injection analysis (FIA) is an excellent technique for analyzing liquid samples which have matrices not tolerated by ICPMS. Samples with large concentrations of dissolved solids may not be analyzed by ICPMS using conventional sample nebulization. Samples containing organic solvents may cause carbon deposits to form on the sampler and skimmer cones, or they may completely extinguish the plasma. FIA circumvents this problem by introducing the sample as a small plug of only a few microliters in volume. A liquid chromatography pump may be

used to deliver the mobile phase to the ICPMS instrument at the standard flow rate of 1 ml min^{-1} . The mobile phase should be a solvent which is compatible with ICPMS such as water or a 2% nitric acid solution. An injector placed between the pump and the ICPMS instrument can be used to introduce the sample into the mobile phase stream as a small plug which is detected by the instrument. Because small sample sizes are used, the plasma distortions should be dramatically reduced. Calibration curves are constructed using peak areas.



Analytical laboratory manager Gerald Thomas with the ICPMS unit at the Center for Applied Energy Research.

ANALYSIS OF SOLID SAMPLES

The analysis of solid samples by ICPMS is challenging. Geological materials such as coal and minerals are difficult to digest, and acid digestion may further complicate the sample matrix increasing spectroscopic and non-spectroscopic interferences. Techniques that allow samples to be analyzed in solid form reduce preparation time and may reduce interferences.

In laser ablation (LA), the solid sample is subjected to a laser pulse. The electromagnetic radiation is converted to thermal, mechanical, chemical and electronic energy at the sample surface. Particles are ejected from the sample surface, and these particles may be swept to the ICPMS instrument by means of a carrier gas such as argon. LA allows samples to be analyzed after little or no sample preparation, and it

provides spatially resolved information. Because particles are swept to the plasma as a dry aerosol, sample transport efficiency is dramatically increased. Ionization in the plasma is more complete since no energy must be used to desolvate the sample once it reaches the plasma. LA systems that are compatible with ICPMS instruments are commercially available. Quantification of trace elements with LA-ICPMS has proven difficult in the past because of fractionation effects. Different elements may have differing ablation rates which are dependent upon the sample matrix. This phenomenon is known as fractionation. Fractionation effects have been reduced with the use of lower wavelength lasers.

Electrothermal vaporization (ETV) may be used for the analysis of small liquid samples or for solid samples (usually in powdered form). ETV involves the heating of the sample on a graphite platform or metal filament that is resistively heated. The vaporized sample is swept to the ICPMS by an inert gas via a transport line. ETV has been used for the analysis of biological materials and geological materials such as coal fly ash. The difficulty with ETV as with all solid sampling techniques is calibration. External calibration with liquid standards or powdered standard reference materials may be performed, and the method of standard additions may also be employed.

The direct sample insertion technique (DSIT) involves the insertion of the sample held by a graphite furnace into the plasma. The high temperatures of the plasma vaporize, atomize, and ionize the sample. Solid sample may also be ground to a fine powder and made into a slurry which can be nebulized into the plasma. Most reports of slurry sample introduction involve the analysis of geological and environmental materials.

ELEMENTAL SPECIATION STUDIES

Liquid chromatography (LC), gas chromatography (GC) and supercritical fluid chromatography (SFC) may be interfaced to an ICPMS instrument to perform speciation. The coupling of LC with ICPMS is easy to perform since the flow rates associated with LC are compatible with ICPMS, and the ICPMS instrument is designed for liquid sample introduction. A simple transfer line of PEEK tubing which connects the chromatographic column to the nebulizer is sufficient. With GC, and

(continued, page 5)

SFC, samples are introduced in gaseous form, so a heated transfer line must be constructed to prevent the condensation of analytes as they travel to the plasma. The nebulizer and spray chamber are not needed, and the transfer line may be connected directly to the base of the torch.

Capillary electrophoresis may be coupled with ICPMS, but this interface is more difficult to achieve. The extremely low flows associated with capillary electrophoresis require that a low flow nebulizer be used. In addition, the electrode must be grounded in some manner since the capillary end leading to the ICPMS is no longer in buffer solution. However, the high resolution of CE coupled with the sensitivity of ICPMS makes a powerful combination for elemental speciation.

CONCLUSIONS

The use of ICPMS does not have to be limited to the analysis of dilute aqueous solutions. Techniques for the analysis of aqueous solutions with complex matrices, solid samples, and small volume samples exist, and as these techniques improve, so will the utility of ICPMS. The challenge to analytical chemists is to continue to improve upon these methods and to develop new ones that will provide sensitivity and precision for the analysis of real world samples.

The author may be contacted at:

ackleykl@mail.uc.edu

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COMMENTARY

A Brief History of the UMWA

Dan Reitz

On January 25, 1890, when two rival coal miners' unions joined ranks to form the United Mine Workers of America, they ended 50 years of conflict over union ascendancy in an industry undergoing rapid growth. The new coal miners' union adopted its slogan from earlier unions - United We Stand, Divided We Fall.

As the industry expanded, the need for union protection was obvious. Coal miners labored 12 to 14 hours each day, loading coal in hazardous conditions. They were paid only for the coal that was loaded and sent to the surface, receiving nothing for hours of laying track, setting timbers for roof support, and clearing rock falls. Some coal operators placed a greater value on the mules hauling coal cars out of the mines than on the men themselves. Young children toiled long hours as breaker boys sorting rock from coal. U M W A President John Mitchell, a legendary figure in union history, led the movement to abolish child labor and to establish the eight-hour day.

Early Battles to Organize

Efforts to organize the union led to bitter mine wars, such as the battle of Blair Mountain in 1921, when UMWA supporters marched 50 miles through West Virginia to confront armed mine guards and state militia. Before labor won the legal right to organize, incidents like Blair Mountain were common, and coal miners known to be sympathetic to the UMWA were jailed, shot, or blacklisted. Miners' families faced eviction from company houses to tent colonies, where unsanitary conditions and the threat of fire prevailed.

For some coal operators, eviction was not enough. In 1914, after being evicted from company housing when they struck for union recognition and a contract, 14,000 UMWA members set up a tent colony in Ludlow, Colorado. Company gunmen and Colorado National Guardsmen fired on the colony with machine guns and torched the tents. Twenty were killed, including eleven children and two women. The incident became known in labor history as the "Ludlow Massacre"

A New Era: John L. Lewis

In 1920, the union changed dramati-

cally when John L. Lewis was elected President of the UMWA. Born the son of a coal miner in Lucas, Iowa, he moved with his wife to Springfield, Illinois in the early 1900s. Lewis was reelected continuously until his retirement in 1960. For forty years, in the coalfields and at the bargaining table, the word of John L. was law.

With Lewis at its head, the UMWA pushed through safety legislation, a guaranteed eight-hour day, a national wage agreement, and industry-wide negotiations. The growth of the young labor movement was speeded by the passage of the 1933 National Industrial Recovery Act, an effort by President Franklin D. Roosevelt to end Depression unemployment. More importantly for the UMWA and other struggling unions, the Act gave working men and women the right to join labor organizations of their own choosing. They did this in droves, swelling membership from 100,000 to 400,000 in one year.

For UMWA members, one of John L. Lewis' greatest achievements was the establishment in 1946 of a comprehensive miners' Welfare and Retirement Fund. He demanded that coal operators pay a royalty on tonnage to finance the fund, which would provide miners and their families with medical care, hospitalization, death benefits, and treatment for the disabled. When the operators refused to comply, Lewis called a national walkout. The government moved to seize the mines, and one week later a contract was signed creating the Welfare and Retirement Fund, providing benefits from the cradle to the grave. This plan served as a model for comparable plans in other industries.

Mechanization of the coal industry, which began in earnest in the 1950s, caused massive layoffs among UMWA members. But Lewis supported the move to mechanize, declaring that increased productivity would provide greater finances for the Welfare and Retirement Fund. However, as employment among members fell from 450,000 to 170,000 thirteen years later, the Fund cut benefits.

The Road to Democracy

Shortly after Lewis retired W. A. Tony Boyle became president in 1963 and attempted to continue Lewis' hard-fisted rule. But, lacking Lewis'

charisma and his ability to win contract demands, Boyle failed to gain strong support from the membership.

In 1969, International Executive Board Member Joseph "Jock" Yablonski challenged Boyle's leadership by launching a campaign for the UMWA presidency. Boyle won the election, but the results were later overturned by a federal court and a new election was ordered. Before it could be held, Yablonski and his wife and daughter were found murdered. Boyle was tried and convicted of ordering the killings and sentenced to life in prison. The rank-and-file responded by electing as UMWA President Arnold Miller, head of the Miners for Democracy movement within the union. Miller brought to the office a new emphasis on democratic reforms.

As coal boomed in the 1970s, the UMWA won cost-of-living increases, sick and personal leave, sickness and accident benefits, and the return of medical coverage for disabled miners and widows. Democratic control of contract ratification was given to the rank-and-

file when a constitutional convention established the right of members to vote on their contracts. In contract battles, the U M WA won the right to have local safety committees inspect the mines and withdraw miners believed to be in imminent danger. In 1974, UMWA members won the contractual right to refuse unsafe work.

But the struggle for mine safety was far from over. Safety legislation was spurred only by disasters such as the explosion on November 20, 1968, at Consolidation Coal Company's No. 9 Mine near Farmington, West Virginia. In that disaster, 78 miners were killed. The next year, Congress passed the historic Federal Coal Mine Health and Safety Act, which set uniform health and safety standards for surface and underground operations.

The Union in the 80s

Arnold Miller resigned as UMWA President in 1979. After an interim president, Richard L. Trumka became president in 1982. During the first year of the Trumka administration, the

U M WA International Union sought increased involvement by the rank-and-file in organizing relief programs for the unemployed and the union's reorganized health and safety program.

The UMWA in the 90s and in the Future

Unemployment remains the most severe problem plaguing the U M WA. Technological changes, coupled with the passage of the Clean Air Act Amendments of 1990, have severely reduced the number of miners. Coal mining is the most dangerous industrial occupation, and lax enforcement of mine health and safety laws is another area of growing concern to the UMWA.

For more than one hundred years, the strength of the United Mine Workers has been its people - the men and women of the coal fields. The mission for its second century is to build upon its first century of pride, commitment, and solidarity to meet the challenge.

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