

# Construction and optimization of the ecological chain of Germanium

*There are some study on construction and optimization the ecological chain of germanium(Ge), which can't combine germanium with ecological chain. Germanium ecological chain is composed of related germanium enterprises, it is s "food chain" composed by different producers, consumers, producers of germanium and other industries, which plays synergistic effect. The basic connotation of germanium ecological chain is "recycling" mechanism. Although the ecological chain of germanium is a closed loop system, it is not a closed system, but an open dissipative system with the exchange of material, energy and information with the outside world. The main source of germanium smelting raw material are lead zinc ore and lignite, therefore, this paper studies the construction of germanium ecological chain from two aspects: the construction of germanium ecological chain and the ecological chain of lignite. Study on the effective interaction between germanium ecological chain and environment respectively from three aspects of material, water and energy cycle.*

**Keywords:** Construction, Optimization, Ecological Chain, Germanium.

## Introduction

There were a lot of scholars studied on construction and optimization the ecological chain of Germanium. ZOU and WANG (2006) introduces the characteristic and the main application of germanium resource, summarizes the distribution and peculiarity of germanium contained in lead-zinc ore and lignite, analyzes the progress of distilling germanium in lead-zinc ore and lignite, and the machining status of common goods and refined goods of germanium [1]. WANG et al. (2014) found that the color of the title crystals (black), which is darker than that of the reported three compounds with chains of germanium clusters, may result from the naked Kand their interactions with the chain. And the structure differences between and the reported three compounds with chains of germanium has also been discussed [2]. Gagan and Brishbhan (2015) shown that a shifted germanium profile eventually evolves into a box-

triangular Ge-profile in the SiGe-base, which could simultaneously minimize the base transit time and reduce emitter delay by virtue of the high current gain [3]. There are other similar related studies too, but they can't combine germanium with ecological chain, this paper researched on structuring and optimizing the ecological chain of Germanium [4-13].

## 1. The Connotation of Germanium Ecological Chain

Germanium ecological chain based on the principles of ecology, to restore and expand the stock of renewable resources and improve the ecological environment for the purpose of improving the productivity of basic resources, designing the link of the germanium industry in the simulation ecosystem according to the needs of society, and to create a new kinds of innovation activities of germanium industrial system. In the chain of germanium ecological chain, the germanium waste of upstream business was used as a raw material supplied to the downstream enterprises. The core of germanium ecological chain is to modeled natural ecosystem production planning activities, through the coupling between germanium enterprises to achieve material and energy recycling cascade. This can reduce the natural ecological system of waste emissions, reduce the impact of human economic activities on the natural ecological system, but also maximize the efficient use of natural resources and reduce the consumption of natural resources. The ultimate goal of germanium ecological chain is to achieve harmonious development between man and nature, achieve a win-win situation of the development of economic system and ecological system.

The connotation of ecology has the following two points:

Firstly, the basic connotation of germanium ecological chain is the thought of "chain". Germanium ecological chain is not single germanium enterprise but the associated enterprises composed of germanium "chain", producers, consumers and disintegrators of different social division of labor from upstream and downstream consist of a "food chain", playing a synergistic effect.

Second, the basic connotation of germanium ecological

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chain is the mechanism of “loop”. The difference between germanium ecosystem and the traditional industrial chain is that it is based on established principles of ecology. Traditional chain is operated with unidirectional linear of the “resources - products - waste”, and operation mode of germanium ecological chain is “germanium resources - products - recycling,” it increases the loop feedback mechanism and aims to improve resource use efficiency and reduce waste emissions so that improve industrial efficiency. So the germanium ecological chain is a closed loop system, it is not a closed system, but an open dissipative system with the material, energy and information exchange.

## 2. Construction the ecological chain of lead and zinc smelting Germanium

The slag and ash of smelting lead and zinc is an important source of the raw materials of the smelting Yunnan germanium. For example, germanium is mainly distributed in the Huize lead-zinc deposit. According to the requirements of the establishment of the ecological chain of the material cycle, energy cycle and water cycle, we can build the Yunnan germanium industry ecological as follows:

### 2.1 THE MATERIALS CIRCULATION OF GERMANIUM ECOLOGICAL CHAIN

The raw materials processed by the lead and zinc metallurgical factory mostly come from the lead and zinc sulfide ore deposits. This ore deposit is often associated with the metal of Ge, as well as Ga, Se, Te, TI, Cu, Bi, Cd, Co, etc. In the beneficiation process, the main element of lead and zinc is difficult to completely separate into the respective concentrates (lead concentrate and zinc concentrate). The distribution of these elements is associated in this

concentrate. Lead and zinc ore processing smelter in addition to the production of the main metal lead and zinc, but also should smelt slag and soot recovered germanium refining, refining other associated metals and making full use of resources.

Waste residue containing germanium and ash can be used to produce the germanium tetrachloride. The other associated metals can enter the respective associated metal refining segment.

Germanium intermediate products and final products will produce waste residues, and these impurities can be used to make bricks and cement, which can be used for the construction industry.

After the scraped of the final product of germanium, when it is repaired and alteration, it can be made of germanium products whose quality and performance are not much bad than new products. This can save natural resources and production cost of germanium. Germanium remanufacturing can be divided into two kinds: one is the restorative remanufacturing; the other is the upgrade of remanufacturing. Arrive restorative remanufacturing is mainly for the physical life and economic life of germanium products. Using the waste of the residual life components germanium as the manufacturing blank, through the advanced technology of surface engineering processing to restore its size and performance. Remanufacturing upgrade is mainly update the products which has reached the life of the equipment and does not conform the current technical innovation principle especially through the use of new materials, new technologies, new processes, etc. to improve and upgrade the equipment technical performance.

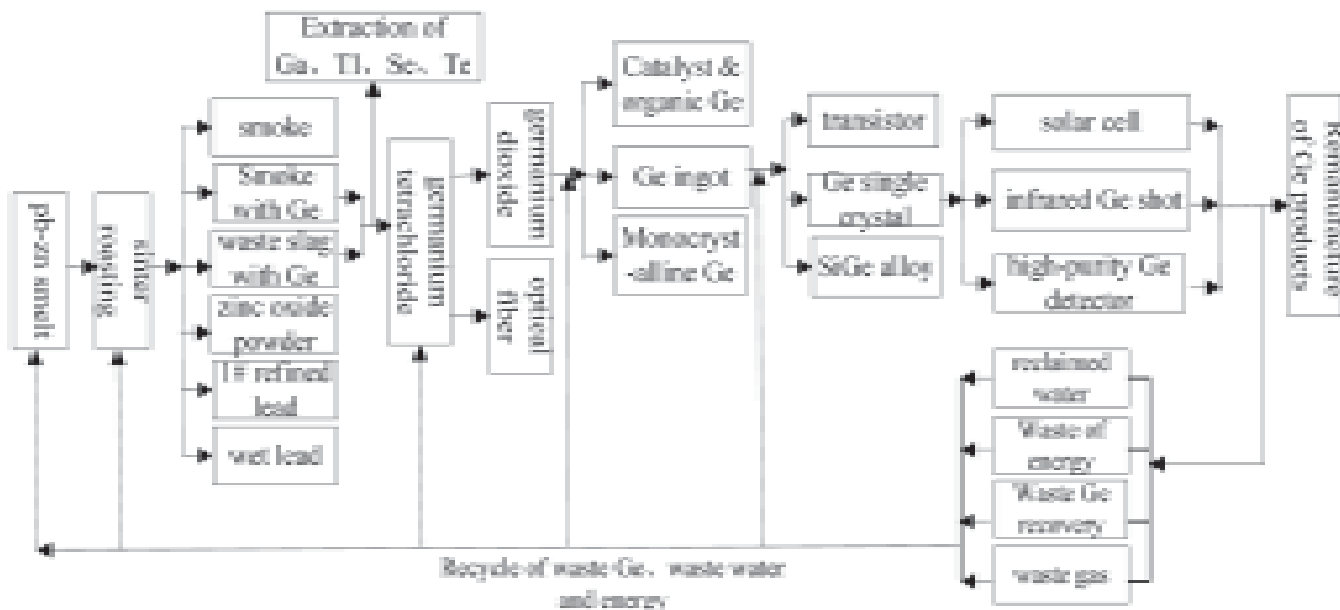


Fig.2 The Ecological Chain of Hydrometallurgical Extraction of Germanium industry

From the point of the current development status, China remanufacturing actively develop the surface technology, and make it successful application in the components of the remanufacturing, and conquer the residual life evaluation, which has made important progress of the development of remanufacturing. The study of the surface technology and life assessment is aimed to improve the utilization rate of the old thing which will have a significant impact on saving energy, saving material to protect the environment. So the future mode in Yunnan of the germanium remanufacturing should be supported by high and new technology, regard the iron utilization efficiency improvement as the core, develop it in a combination of research approaches, which is circulation and the economy.

As for the germanium materials which can't be remanufactured, they shall be recycled, and on the basis of their physical and chemical properties and classifies the composition proportion, and then determine which link should they return as the input materials. In the process of recycling, we should try to put these materials into on middle and lower reaches of the link to reduce unnecessary repeat refining and processing.

## 2.2 THE CYCLE OF FILLING WATER

The production and processing link of germanium chain will consume large amounts of water. The water come into the production process, and finally will discharge as the waste water. The discharge of waste water of each link can be recycled to reduce emissions and pollution.

The wastewater contained a lot of pollutants, which can be purified making it become more clean "water". The water can be used in other production and processing link. The recycled water is not drinkable, but it can be used in the places that water quality requirement is not high, such as flush toilets, car washing and spraying roads, landscaping, etc. Reclaimed water engineering can be thought of as a life between the building water supply and drainage system between the miscellaneous water supply technology.

## 2.3 THE USAGE OF ECOSYSTEM ENERGY

The smelting of associated production of lead and zinc and the smelting, purification, production and processing germanium of the germanium are all large energy consumption industrial. The energy can't be directly discharged, which is a waste of energy. It not only affects the air and the environment, but also will increase production costs. Yunnan should develop energy recycling technologies to minimize energy waste, to reduce the costs and improve the production efficiency.

### 3. Construction the ecological chain of distilling Ge from lignite

At Lincang Yunnan, germanium are mainly distributed in the lignite, so we according to the technological process of

extracting Ge from Lignite, construct the ecological chain of extracting Ge from Lignite.

#### 3.1 THE ECOLOGICAL CHAIN OF THE METHOD OF HYDROMETALLURGY TO DISTILL THE GE IN THE COAL

The method of hydrometallurgy to distill the Ge in the raw coal, is to breaking the raw coal to a certain size. Direct leaching distillation from the solution which not less than 7 mol hydrochloric acid, and distilling the Ge in the coal.

The method of this technological process is simple, and the recovery rate of Ge in the coal is higher, generally can reach more than 90%, but the dosage of hydrochloric acid is too large, industrial production's cost is too high, so we also need to do some experimental study to realize the industrial application of the economy. Ge in coal is mainly forms chemical combination with organic matter, humic acid complex and germanium organic compounds. So if we can use the method of coal washing to remove most of the coal gangue in the coal, the cost of using the method of hydrometallurgy directly from the leaching of germanium in coal will be greatly reduced.

The ecological chain of distilling Ge from Lignite are shown in Fig.2:

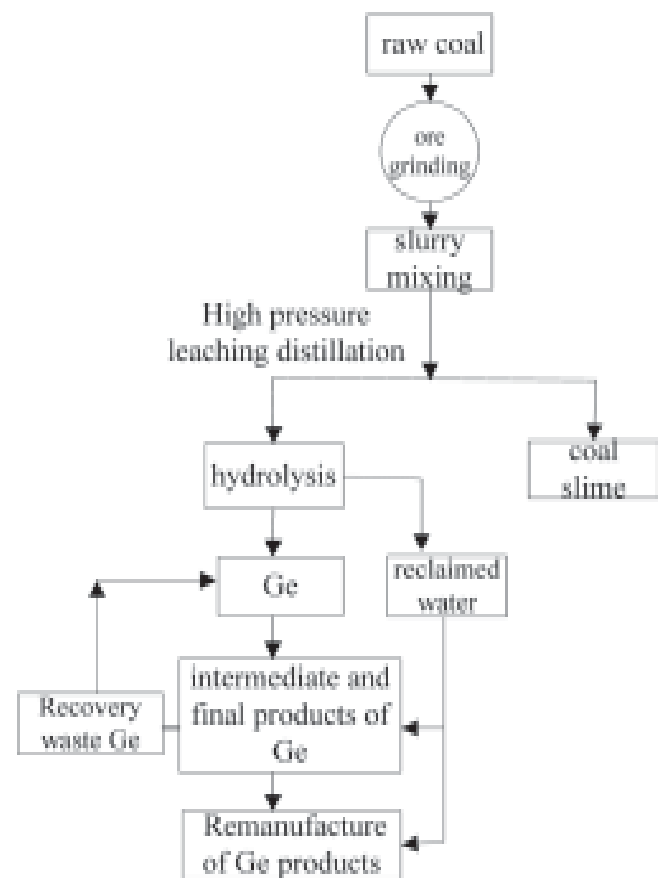


Fig.1 The ecological chain of Germanium

### 3.2 THE METHOD OF FIERY METALLURGY TO EXTRACTION GE FROM LIGNITE

The method of fiery metallurgy to Extraction Ge from Lignite, it means extract the Ge from coal's combustion products after coal are burnt. At present, Yunnan also use the by-products of burnt coal as the main production material of germanium, such as coal ash, fly ash, coal tar and waste ammonia water of coking plant. Recovery the germanium from the byproduct of burnt coal, basically has the following several ways:

#### (1) Alloy Method

We use the chalcophile affinity and siderophile affinity of germanium to reduction smelting, make the germanium into the copper alloy and achieve beneficiation, and then recovery the germanium from the copper alloy.

The alloy method is simple, it is good for dealing with the coal which contain more coal ash, the recovery rate of germanium are nearly 50% when in terms of the content of germanium in coal.

The ecological chain can be constructed as shown in the figure below.

#### (2) Method of Volatilize Ge Again

After the coal are burnt, the beneficiation of germanium in coal dust or ash is about 10 times, and the content of germanium could reach 0.1% ~ 0.3%. This material with Ge should not be directly used to extract Ge, it need to be briquetted and be volatilized again in the blast furnace or shaft furnace, and then recovery the germanium from the secondary dust which are rich in germanium. This method is called method of volatilize Ge again.

This method is simple and with higher rate of beneficiation, it can get germanium concentrates or

germanium quickly. The disadvantages of this method are more loss of Ge, the total recovery rate not higher than 70%~70%, large energy consumption and easy to produce iron after twice volatile treatment of fire and smelting process, lead to more decentralized of Ge.

The process of volatilize Ge again method to construction the ecological chain is as follows:

#### (3) Alkali fusion – neutralization method

It is better to use the alkali fusion – neutralization to deal with the coal ash which rich in Ge, namely oxidizing melting with NaOH or Na<sub>2</sub>CO<sub>3</sub> under the 900°C and then the Ge in material was transformed into germinate.

The Ge and in the material will into Alkali soaking liquid when leaching of smeltdproduct with hot water. After hydrolysis the differences of PH, first use hydrochloric acid neutralization to the conditions with 0.2 mol/L residual alkali, then precipitate the and , and remove them, use hydrochloric acid neutralization it to PH5, precipitate Ge in form of GeO<sub>2</sub>·nH<sub>2</sub>O. Since then distill Ge by chlorination distillation of this precipitate matched with hydrochloric acid and sulfuric acid.

This method use the neutralization process for many times, acid-base cost is large, the operation of liquid-solid separation is more, and germanium recovery rate is about 75%~83% of germanium in coal.

The process of this method to construction the ecological chain is similar with alloy method.

#### (4) Leaching method with hydrofluoric acid

Above these three methods, the recovery rate of germanium in coal is not high, this is because the combustion

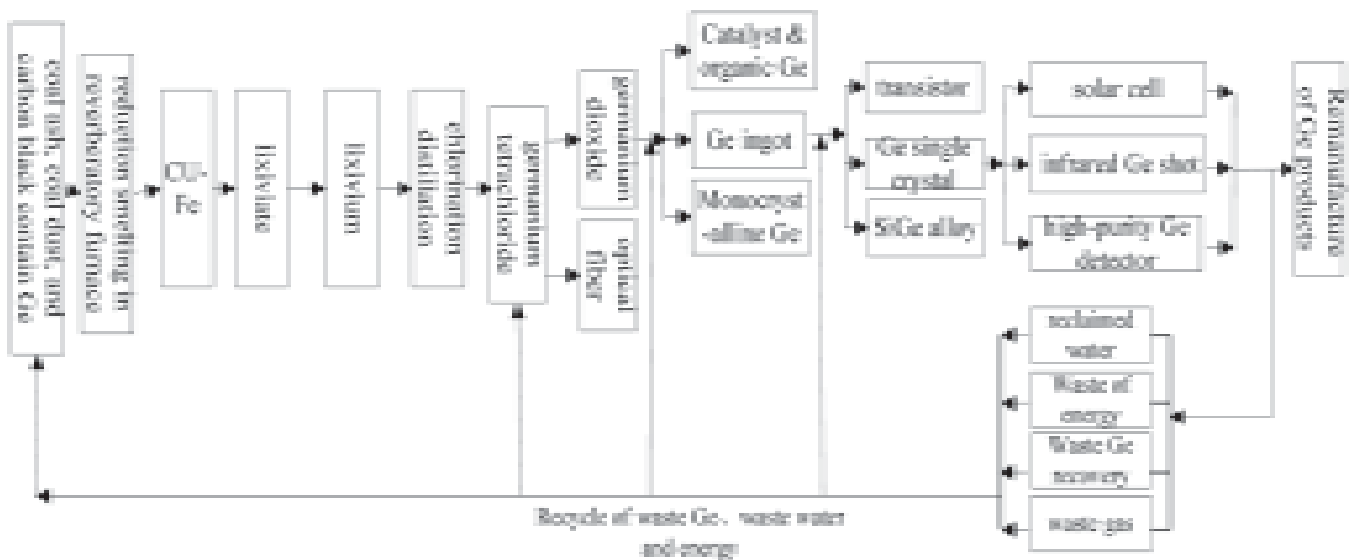


Fig.3 The Ecological Chain of Fire Extraction of Germanium

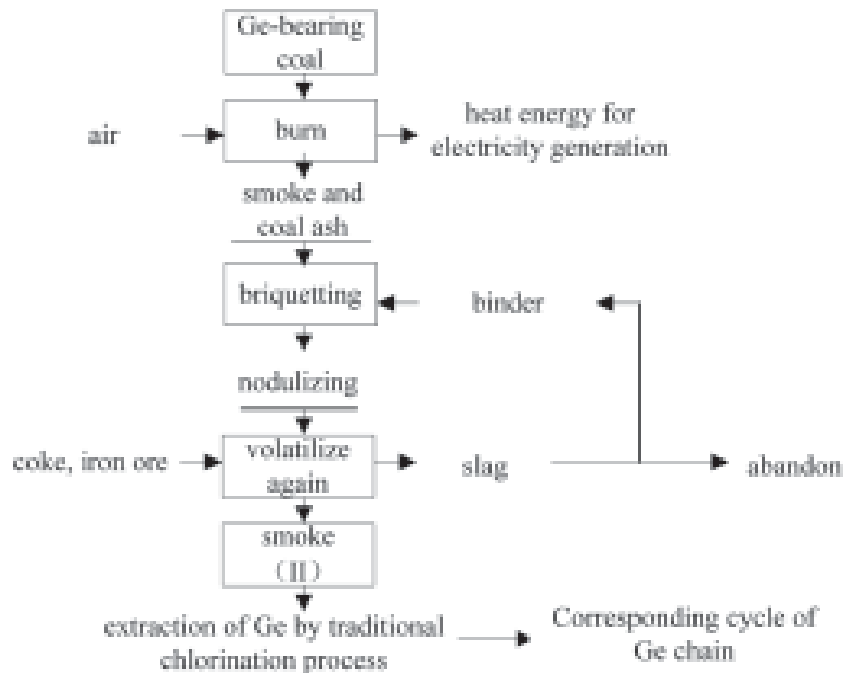


Fig.4 The ecological chain of extracting Germanium from volatile Germanium again

of coal is a high temperature oxidation process, now in addition to the part of germanium into  $\text{GeO}$  and volatilizes into smoke, most of the germanium in the solid forms of germanate and into coal ash. Directly use the traditional chlorination distillation extraction germanium from the coal ash of burnt coal, it is difficult for germanate or solid solution of to be dissolved by acid. With 4~6 mol/L hydrochloric acid, there are only 25%~60% of germanium can be dissolved from the products above, but the amount of germanium will be less if we use sulfuric acid, generally less than 25%~40%. Add the fluorine compound when acid leaching, can prompt the decomposition of germanate and solid solution of , decomposition of germanium turn into complex germanium fluorine, and enter into the pickle liquor. So there are someone put forward the leaching method with hydrofluoric acid on the basis of this principle. This method can strengthen the leaching of germanium from high temperature burning coal ash and similar materials, high leaching rate, process short, but there are problems of equipment anti-corrosion and waste liquid return to use with defluorination. The method to construction the ecological chain is similar with above.

### 3.3 EXTRACTION METHOD TO EXTRACT GERMANIUM IN COAL

For hydrometallurgy and fire smelting method to extract germanium from coal, the problem of high cost and low recovery etc, while more research about the solvent extraction method to extract germanium in coal at home and abroad in recent years and has also get progress in this aspect. There have a wide variety of extraction, such as carbon tetrachloride, kerosene, methyl isobutyl ketone (MiBK), alpha hydroxy

(LIX-63), diethyl ether, amine extraction, monoalkyl phosphate extraction agent (P204) and synergistic extractant YW100, 8-hydroxyquinoline extraction agent (kelex-100) and so on, especially the effect of 8-hydroxyquinoline extraction agent (kelex-100), alpha hydroxyoxime (LIX-63) extraction is better. But these two kinds of extraction has the problem of limitation of using conditions and lack of raw materials at home, so they need to import from other countries. It requires our country's scientific workers based on our own national conditions, and the research of efficient extraction agent should suit for national conditions. It is reported that our country has researched the synthesis chelating extraction agent of new effective (dihydroxamic acid) and has a better extraction.

Apart from the above methods, the ways of extracting germanium in coal has also include ion exchange method, tannin precipitation etc. Although there have many methods, but they have many problems, for instance, the recovery rate is not high, the process is relatively complex, the cost is high and the product purity is insufficient. In our country the germanium ore resources is scarce, while we have the high  $\text{GeO}_2$  reserves in coal, and China's coal reserves comes first in the world, so germanium extracted from coal should be promising and economic value. Therefore, pay more attention to the study of comprehensive utilization of coal and increasing the comprehensive recycling of scattered elements in coal, not only has it a great significance to develop our country's scarce metal business, but also to realize the sustainable development of coal industry of China in the 21 century. The construction of the ecological chain for extraction of germanium is similar to hydro-metallurgy method.

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