Ge in Coal and Coal-Ge deposits in China

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Abstract: Coals are not only fossile energy, but also important industrial materials of usful minor elements. In China, two most important coal-germanium deposits are found in brown coals in Yunnan province and in Inner-Mongolia Autonomous Region. But most coals in China have low concentration of Ge. Its average values in China, America, Australia, Britain and Former Soviet Union are as follows: 3.6×10^{-6}，5.7×10^{-6}，2.9×10^{-6}，4.4×10^{-6}，1.5×10^{-6}. As the content of germanium in coal reaches more than 100×10^{-6}, the Ge has the possibility to be utilized economically. The coal-germanium ore deposit in Yunnan province lies in the Cenozoic Lincang basin, and the coal-germanium ore deposit in Inner Mongolia Autonomous Region is in the Mesozoic Shengli basin. In Lincang coal basin of Yunnan province, the values of some coal samples were up to or higher than 3000×10^{-6}. Most of Ge in coal is combined with the organic or is adsorbed in the organic matters. The brown coals of Sheng Li coal mine in Inner-Mongolia contain Ge, and its content ranges from 135×10^{-6} to 1530×10^{-6}. The total reserve reaches to 3431 tons in this coal mine. This kind of coal-Ge deposit in Inner-Mongolia is being studied and the result shows very bright prospect. It is the biggest Ge-coal deposit found in the world and it has been found only a few years ago. Another big coal-Ge deposit in Yimin is being researched, and It may be the biggest Ge reservoir in China. It is important to know well about the elements in coal, especially the coals contain elements of industrial value.

Keywords: Germanium in Chinese coal, Inner Mongolia Autonomous Region, Coal-Ge deposit

1. Abundance of Ge in Chinese coal

Goldschmidt found that coal contained Ge in 1930. In 1933, Goldschmidt and Peters proved that the abundance of Ge had reached to 1.1 percents in bituminous coal ash in Dalemen mine of England, and then it became possible to extract Ge from coal ash. In 1950s, many countries, such as England, America, Australia, Japan, Former Soviet Union and so on, put the emphasis on the investigation on Ge in coal[1-6].China also paid attention to it at the beginning of 1960s, and then the content of a seminar on theoretical issues of Ge in coal published in the academic journal from 1963 to 1965. Ge is a useful element in coal, which was studied at the earliest time and most.

All the coal in nature contains Ge. Only under special geological conditions can Ge be accumulated in coal to become deposit. The abundance of Ge is quite low in most of coal. The distribution of Ge in coal measures is very unstable. Except the big change of Ge in abundance on the plane, its differences appear among different coal measures in the same mine, among different seams in the same coal measures, among different coal rocks in the same coal measures. It is well-known that Ge always accumulates at the bottom of coal measures strata; the content of Ge in the thin coal measures is more than that in thick one; also in the seam on the top of coal measures; the content of Ge in vitrain and brights is more than that in other coal lithotypes.

Table 1 shows the abundance of Ge in the main coal fields in China[7]. These data reflect the contents of Ge in coal in Carboniferous-Permian in North China, Permian in South China and Jurassic in West China. In Tertiary lignite Basin in Yunnan Province, there is coal containing germanium, and in Lincang Coal Basin, oversize ore deposit has been discovered. Table 4 shows the analytical result of coal samples in Lincang coal basin[8]. Abundances of Ge from Lincang coal samples are especially high up to 3000 mg/kg.

Based on analytical data from 3084 samples, abundance of Ge in Chinese coal ranges from 0.5 to 10 mg/kg with the average 4 mg/kg; and in some coal samples, more than 20 mg/kg in abundance; If the value is up to n×100 mg/kg, it is abnormal high one. With the reference of values in foreign coal samples, abundance of Ge in coal in nature is less than 10 mg/kg with the average 5 mg/kg. When abundance of Ge in coal ranges from n×10 to n×100 mg/kg, it would

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be believed abnormal. Some people suppose that the value higher than 100 mg/kg is rich; others pay attention to 20 mg/kg in abundance. Researchers from Former Soviet Union detected the highest value of abundance of Ge was 6000 mg/kg.

2. Occurrence of Ge in coal

Detailed study on occurrence of Ge in coal has been done a lot at home and abroad. The consistent view is that the main occurrence of Ge in coal is in combination with organic matters. But when it comes to the specific methods of combining between Ge and organic matters, different scholars have diverse opinions. Most researchers suppose that Ge combines with organic matters and then turns into Ge complex and Ge organic compounds. Ge always accumulates in the coal of low rank within developed side chain and functional group, It has lower ordering degree. Coal containing Ge with commercial value is almost lignite. Ge that occurs in adsorption states can be adsorbed into organic matters, as well as clay minerals. Few Ge can be found in sulfide and silicate minerals[9-11].

3. Geological factors of Ge enrichment in coal

The content of Ge in coal of Yunnan Province in China is abundant and variable, and the study on these samples is much more[9-14]. Based on the research achievements on Ge in coal of Yunnan Province, the geological factors of Ge enrichment are as follows:

The formation of coal containing germanium needs two necessary conditions: abundant germanium fountain and favorable depositional environment. The first source of Ge is mother rock in sediments. The basement of western Yunnan Cenozoic Basin with the coal containing germanium is granite that can supply enough germanium fountains. The climate of coal-forming period was warm and wet, and it was beneficial for granite weathering, Ge from leaching became abundant germanium fountain. The second source of Ge is hydrothermal solution. In western Bangmai basin, the Ge was transported into swamps by hydrothermal solution.

The so-called favorable sedimentary environment means that the basin stays at the slow subsiding tectonic setting and stable sediment environment, the paleotopography is flat, the development of hydrographic net is slow, the chemical weathering of source rocks is sufficient; advantageous topography and hydrographic and geologic conditions, the solution containing Ge drainage into coal-forming basin; blocked strong reduction environment, the gelation of coal-forming plants and chemical associations and adsorptions with Ge in the solution.

In western Honghe-Yuanjiang fault zone of Yunnan Province, especially on Yunxian-Lincang-Menghai belt and two south-north trending stripes of Tengchong-Luxi-Ruili belt, it generated coal containing Ge in Cenozoic basin on the basis of the above two necessary geological conditions. However, in 122 basins of western Yunnan, there are few basins that exist coal containing Ge with commercial value. Because of possessing optimized combination of two geological conditions, there is peculiar super-large germanium ore deposit in Bangmai basin in Lincang, and its proved reserves of Ge is high up to 800 t .

4. New-found coal-Ge deposit in Shengli coal mine of Inner-Mongolia

Ge contents of 200 coal samples taken in coal seam No.6-1 from Shengli coalfield in Inner-Mongolia ranges from 135 to 1530 mg/kg. This coal bed formed in early Cretaceous. The thickness of this coal bed varied from 0.82 m to 16.66 m with the average of 9.88m. In addition, the depth of this coal bed ranges from 4.25 m to 61.28 with the average 22.46m[15]. It could be mined with open pit. This coal bed has simple structure as there is only one thin carbon-rich mudstone layer. The roof rocks of the coal bed are sandstonse, pebbles and siltstones and the bottom rocks are black shale and mudstone and siltstone. The sedimentary environment of the coal series is alluvial facies that was controlled by the marginal fault during its deposition. The area with the richest Ge in No.6-1 coal seam is 1.64 km^2. According to the assessment of the local geological bureau, the Ge reserve reaches to 3431 ton. That is the biggest coal-Ge deposit in the world.

Another coal-Ge deposit is found in Cretaceous lignite in Yimin coal field, in which the Ge abundance reaches to 150 mg/kg in dozens of coal samples from No. 12 coal seam. Soon we will obtian more information about this coal-Ge deposit.

The occurrence of germanium was investigated using five steps sequential chemical extraction method [15]. The result indicated that germanium is in primarily chelated-humic acid combined with other organic compound which formed fastness chemical bond in this germanium deposit of coal. Some part of Ge assumed adsorbent state, few part of Ge consists in silicate mineral lattice with isomorphism state.

The Ge enrichment and its geological factors in Shengli and Yimin coal fields, Inner Mongolia have

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great differences with those in Lincang County, Yunman Province. More Ge-deposits may be found in the further general investigation and exploration in Erlian basin group.

Table 1 Ge in coal in the main coalfield (diggings) of China

province	*coalfield (diggings,mine)*	*coal-forming age (horizon)*	*kind of coal*	*number of samples*	*bound W(Ge)/mg · kg⁻¹*	*arithmetic mean W(Ge)/mg · kg⁻¹*	*geometric mean W(Ge)/mg · kg⁻¹*	*data sources*
Hebei	Tangshan Jingge village	C-P	QM	1	2.99			Zhuang(1999)
Shanxi	Pingshuo Antaibao mine	C-P(Taiyuan formation)	QM	8	0.49 ~ 0.78	0.61	0.56	Zhuang(1998)
Shandong	Yanzhou diggings	C-P	QM-FM	26	0.44 ~ 11.52	5.9	4.9	Liu(1999)
Shandong	Jining diggings	C-P	QM	30	1.69 ~ 9.11	5.1	4.5	Liu(1999)
Shandong	Tengxian diggings	C-P(Taiyuan formation)	QM	553	~ 80.0	6.1		Li(1991)
Shandong	Tengxian diggings	C-P(Shanxi formation)	QM	293	~ 17.18	1.8		Li(1991)
Shandong	Chaili mine	P (Shanxi formation)	QM	1	1.6			* (1994)
Shandong	Zaozhuang mine	C-P(Taiyuan formation)	PM	1	1.5			* (1994)
Jiangsu	Xuzhou mine	C-P(Taiyuan formation)	QM	1	2.1			* (1994)
Jiangsu	Xuzhou mine	P (Shanxi formation)	QM	1	1.7			* (1994)
Anhui	Huaibei coalfield	P (Shanxi formation)	QM-WY	7	1.2 ~ 4.30	2.3	2	* (1994)
Anhui	Huaibei coalfield	P (Shihezi formation)	QM-WY	5	1.7 ~ 4.3	3	2.8	* (1994)
Guizhou	Shuicheng Wangjiazhai mine	P_2 (Longtan formation)	QM-FM	3	0.47 ~ 4.75	1.27	0.76	Zeng(1998)
Guizhou	Liupanshui area	P_2 (Longtan formation)	QM-WY	32		3.06		Ni(1998)
Guizhou	Shuicheng NO.11 seam	P_2 (Longtan formation)	QM			2.54		Ni(1998)
Guizhou	Shuicheng NO.11 seam	P_2 (Longtan formation)	FM			2.33		Ni(1998)
Guizhou	Shuicheng NO.11 seam	P_2 (Longtan formation)	JM			7.66		Ni(1998)
Guizhou	Liuzhi&Shuicheng	P_2 (Longtan formation)	QM-WY	45	0.4 ~ 3.4	1.7		Zhuang(2001)
Yunnan	eastern diggings	P_2 (Xuanwei formation)		1334	0~ 22.0	3.66		Zhou(1985)
Shanxi	Datong NO.1 mine	J_1 (Datong formation)	RN	8	0.16 ~ 3.06	0.76		Zhuang(1999)
Inner Mongolia	Yimin pasture	J_3	HM-YM		~ 450	15		Liu J(1992)
Inner Mongolia	Xilinhaote	J_3-K_2	HM		135.0 ~ 820.0	244		Yuan(1999)
Eerduosi	Eerduosi Basin	J_2 (Yan'an formation)				0.9	1.8	Liheming(1993)
Eerduosi	Shenfu-Dongsheng diggings	J_2 (Yan'an formation)	CY	723	0.1 ~ 22.3	2.11		Dou(1998)
Inner Mongolia	Dongsheng	J_2 (Yan'an formation)	CY	18	0.00 ~ 7.0	2.8	2	Liheming(1993)
Ningxia	Majiatan	J_2 (Yan'an formation)	CY	6	1.00 ~ 11.4	3.47	2.46	Liheming (1993)
Gansu	Huating	J_2 (Yan'an formation)	CY	3	0.37 ~ 4.43	2.15	1.4	Liheming(1993)
Shanxi	Binxian	J_2 (Yan'an formation)	CY	2	0.43 , 2.94	1.69		Liheming(1993)
Shanxi	Diantou	J_2 (Yan'an formation)	CY	8	0.00 ~ 4.70	1.8	1.24	Liheming(1993)
Shanxi	Yuhenggong area	J_2 (Yan'an formation)	CY	11	0.00 ~ 15.00	5.9	5.42	Liheming(1993)
Liaoning	Fuxin Haizhou mine	K_1 (Fuxin formation)	CY	6	0.2 ~ 0.9	0.45		Querol(1997)
Yunnan	Luxi	N	HM		20.0 ~ 800.0			Zhou(1985)
Yunnan	Cangyuan	N	HM			56		Zhou(1985)
Yunnan	Tengchong	N	HM		~ 1730.0			Zhou(1985)
Yunnan	Lincang	N	HM	13	< 0.3 ~ 1470.0	565.8	199.6	Zhuanghanping(1997)
Yunnan	Lincang Bangmai mine	N	HM	1	> 3000			* (2000)
Yunnan	Xiaolongtan mine	N	HM	3	0.33 ~ 1.36	0.85	0.67	* (2000)
Guangdong	Maoming	E_3	HM		8.0 ~ 14.0			Lao(1994)

SA: * ——from the analytic data of the author of this paper.

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