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CHARACTERISTICS AND COMPREHENSIVE UTILIZATION OF OIL SHALE OF THE UPPER CRETACEOUS QINGSHANKOU FORMATION IN THE SOUTHERN SONGLIAO BASIN, NE CHINA

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Abstract. *The Songliao Basin is a large Mesozoic oil shale-bearing basin in northeastern China, the resources of which are most abundant, while the rock's discovered resources are mainly concentrated in the southern part of the basin. The oil shale of the Cretaceous Qingshankou Formation (K_2qn^1) in the southern Songliao Basin was evaluated based on proximate and geochemical analyses. The K_2qn^1 oil shale is characterized by a shallow burial depth, medium-to-high oil yield, medium calorific value, high ash yield and low sulfur content. The maximum oil yield is 16.37% (avg. 5.54%), the calorific value is up to 10,174 J/g (avg. 3,264 J/g), and the average ash and sulfur contents are 82.03 and 1.49%, respectively. In addition to rich organic matter, the K_2qn^1 oil shale contains clay minerals, quartz and feldspars with the respective average contents of 55.0, 23.3 and 12.4%. The contents of chemical compounds SiO_2 and Al_2O_3 are high, being on average 51.58 and 15.02%, respectively. The oil shale is enriched in trace elements Mo, U and Pb, whereas rare earth elements (REEs) are represented by La, Ce, Pr, Nd, Sm, Gd and Tb. In view of the above diverse characteristics of oil shale and in consideration of environmental factors, an economical and efficient scheme of comprehensive utilization of K_2qn^1 oil shale has been proposed. Oil shale can be directly used to refine shale oil by pyrolysis or combusted for power generation, while the remaining ash can be used for producing synthetic marble, building materials, alumina and silica and extracting metal elements.*

Keywords: *Songliao Basin, Qingshankou Formation, oil shale characteristics, comprehensive utilization.*

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1. Introduction

Oil shale is commonly defined as a fine-grained sedimentary rock containing organic matter that yields substantial amounts of oil and combustible gas upon pyrolysis [1, 2]. The nationwide oil shale resources evaluation that was carried out from 2003 to 2006 indicates these resources in China to be abundant: total oil shale resources are 719.9 billion tons, of which oil shale resources of the Songliao Basin are estimated at 323.66 billion tons, 45% of China's total oil shale resources representing 15.41 billion tons of in-place shale oil [3]. In recent years, several large oil shale deposits have been discovered in the southern Songliao Basin; according to the data of the Geological Archives of Jilin Province, China, the total discovered oil shale resources are estimated at 106.25 billion tons, making 92.5% of the national discovered oil shale resources. The discovered oil shale resources of the Qingshankou Formation are estimated at 65.94 billion tons, with a minimum burial depth of 144 m. Therefore, the development and utilization of oil shale in this formation is imperative. However, the oil shale exploitation in the Songliao Basin remains still in the initial stage, while its development potential is not yet quite clear and comprehensive utilization plan has not been worked out.

Shale oil can be obtained from oil shale by pyrolysis and can be used for extraction of gasoline and diesel or for further processing [1, 2, 4]. China is the biggest unconventional shale oil producer, approximately 40% of the world's shale oil is produced in this country [5–7].

Oil shale and semicoke can be combusted in boiler to produce electric power and heat [8–9]. Although shale oil refining and combustion technologies are quite well developed, there are two major problems that currently hinder the development of oil shale industry: low resource utilization rate and environmental pollution [10–12]. Therefore, the comprehensive use of oil shale has attracted increasing public attention [13–16]. In the processes of refining and combustion of oil shale, large amounts of ash are produced, accounting for 60–80% of oil shale production [17]. Discarding or burying the ash not only wastes resources but also has adverse effects on humans and the ecological environment as a whole [8, 18–20]. The oil shale ash left after refining or power generation contains calcite, dolomite, quartz, feldspars and clay minerals, mainly SiO_2, Al_2O_3, and metallic elements, which can be used in the chemical and building materials industries [21–23], to produce nano-Al_2O_3 and nano-SiO_2 [24–27], extract metallic elements [28, 29], and prepare cement and ceramsite [25, 30, 31]. Comprehensive oil shale processing designs can improve the efficiency of resource utilization, perfect the effectiveness of the process and reduce pollutant emissions [9, 32]. This paper discusses the characteristics and comprehensive utilization potential of oil shale of the Upper Cretaceous Qingshankou Formation based on petrological, mineralogical and geochemical data about two sampled core profiles located in the southern Songliao Basin. The study aims to find the most feasible and economical method of comprehensive utilization of oil shale.

2. Geological setting

The Songliao Basin, located in northeastern China, is approximately 260,000 km^2 in area. This Meso-Cenozoic, large and composite sedimentary basin with a fault-depression dual structure represents an essential oil and gas production base in China [33–36]. Based on the basement and regional geological characteristics of the cap rock, the Songliao Basin can be divided into six first-order tectonic units (Fig. 1): the Western Slope, the Southwestern Uplift, the Southeastern Uplift, the Central Depression, the Northeastern Uplift and the Northern Plunge [37–39]. Oil shale is mainly distributed in the Southeastern Uplift, Northeastern Uplift and Central Depression zones [40].

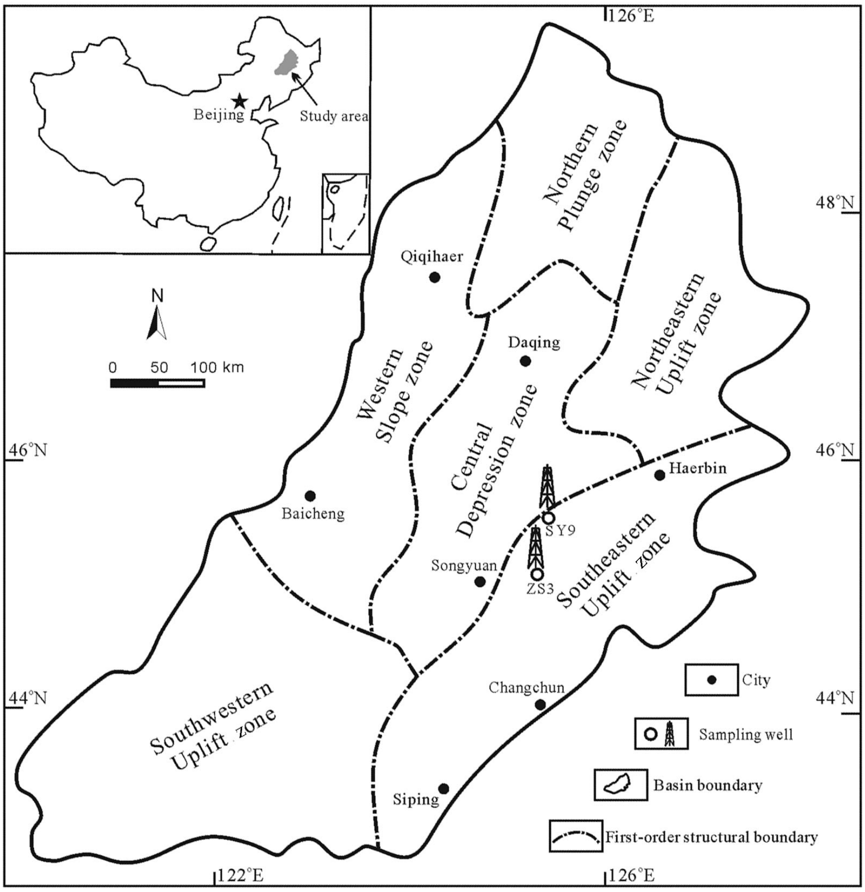

Fig. 1. Location and division of structural units of the Songliao Basin.

The sedimentary cover of the Songliao Basin is composed of Mesozoic-Cenozoic strata. The total thickness of the basement is more than 10 km [37, 39]. After the Lower Cretaceous DengLouku Formation was formed, extensive subsidence took place in the Southeastern Uplift zone. As a result, the Lower Cretaceous Quantou Formation and the Upper Cretaceous Qingshankou, Yaojia and Nenjiang Formations were developed in the depression period, predominantly composed of terrigenous clastic rocks of fluvial and lake facies (Fig. 2). The oil shale in the Songliao Basin is mainly concentrated in the Upper Cretaceous Qingshankou (K_2qn) and Nenjiang (K_2n) Formations [35, 40].

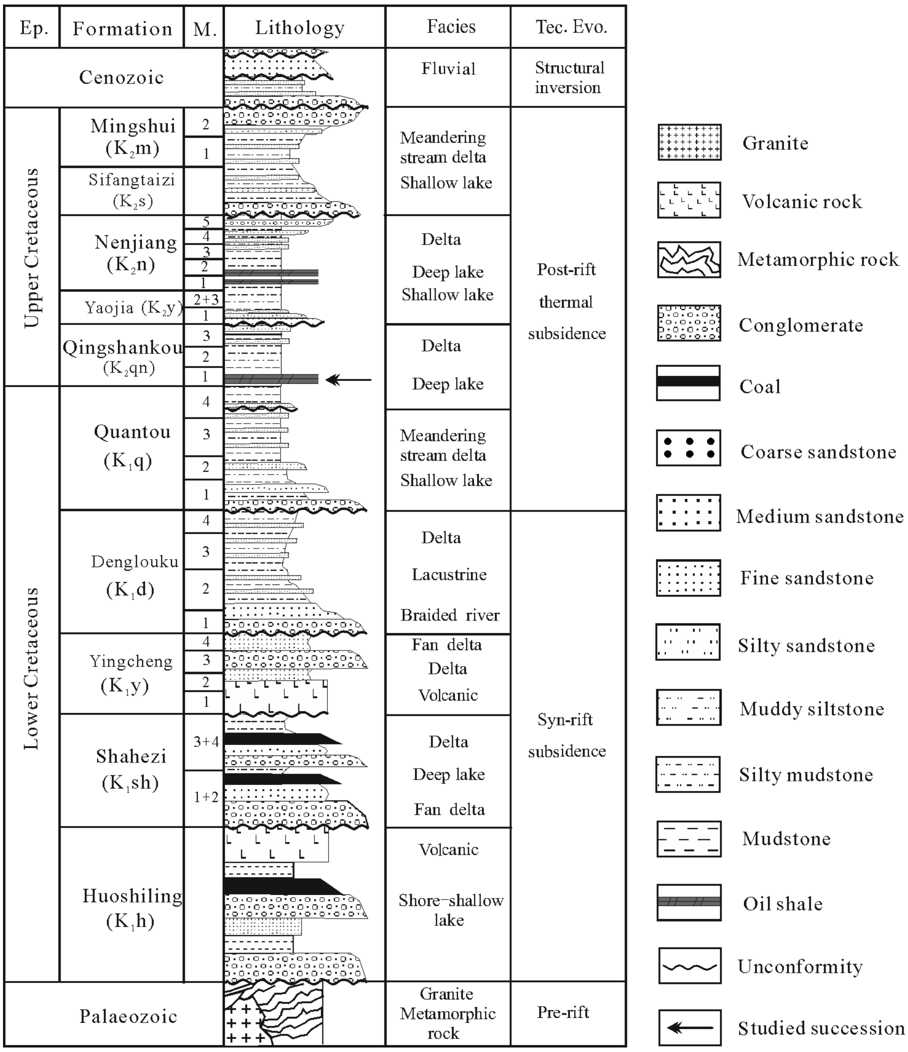

Fig. 2. Stratigraphic column of the Songliao Basin (modified according to [37]). (The abbreviations used: Ep. – Epoch; M. – Member; Tec. Evo. – Tectonic evolution.)

The Qingshankou Formation is divided into three members based on lithology (Fig. 2), of which the first member (K_2qn^1) represents the main period of oil shale development and is also the focus layer of this study. K_2qn^1 incorporated a large lake area during the sedimentary period and developed semi-deep to deep lake facies, with a lithology of mainly grey-black and dark grey mudstone in combination with oil shale, which was mainly formed in semi-deep to deep lake facies.

3. Samples and methods

The samples for the study were taken from wells SY9 and ZS3, which were separately drilled by the Jilin Oil Field of PetroChina Company Limited in 2007 and 2014. Altogether 19 oil shale samples were collected from the two wells, including 3 samples from well SY9 and 16 samples from well ZS3 (Fig. 3). The samples were used for determining oil yield, calorific value, contents of total sulfur, as well as trace and rare earth elements (REEs), and for performing proximate analysis. Based on the test results, 8 samples were chosen for mineral and chemical composition tests.

Oil yield, calorific value and total sulfur determinations as well as proximate analysis were performed in the Key Laboratory for Oil Shale and Paragenetic Energy Minerals of Jilin Province, China. Oil yield gained from low-temperature carbonization at approximately 520 °C was measured by a Chinese Fushun retort using the Fischer assay. The mixture of oil and water was extracted from oil shale by heating, and the content of oil was obtained by weighing the water distilled from the mixture. Afterwards, the oil yield was calculated from the total weight.

Calorific value and total sulfur determinations and proximate analysis were separately carried out using an SDC5015 Calorimeter, an SDS616 Sulfur Determinator and an Xl-2000 Muffle Furnace (all Sande Technology Co., Ltd, Hunan Province, China).

The mineral composition was determined using X-ray diffractometry (XRD) at the Center for Scientific Test of Jilin University, China. A Philips PW1830 diffractometer system with Cu-Kα radiation was used for XRD measurements on pulverized samples (≤ 200 mesh).

The major element oxides, as well as trace and rare earth elements were determined using a Philips PW2404 X-ray fluorescence (XRF) spectrometer and a Thermo Scientific X-series high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) at the Beijing Research Institute of Uranium Geology, China, following the criteria of GB/T14506.28-93 and DZ/T 0223-2001, respectively [41, 42]. The discrepancy between the triplicates was less than 5% for all the elements. Analyses of standards were in agreement with the recommended values.

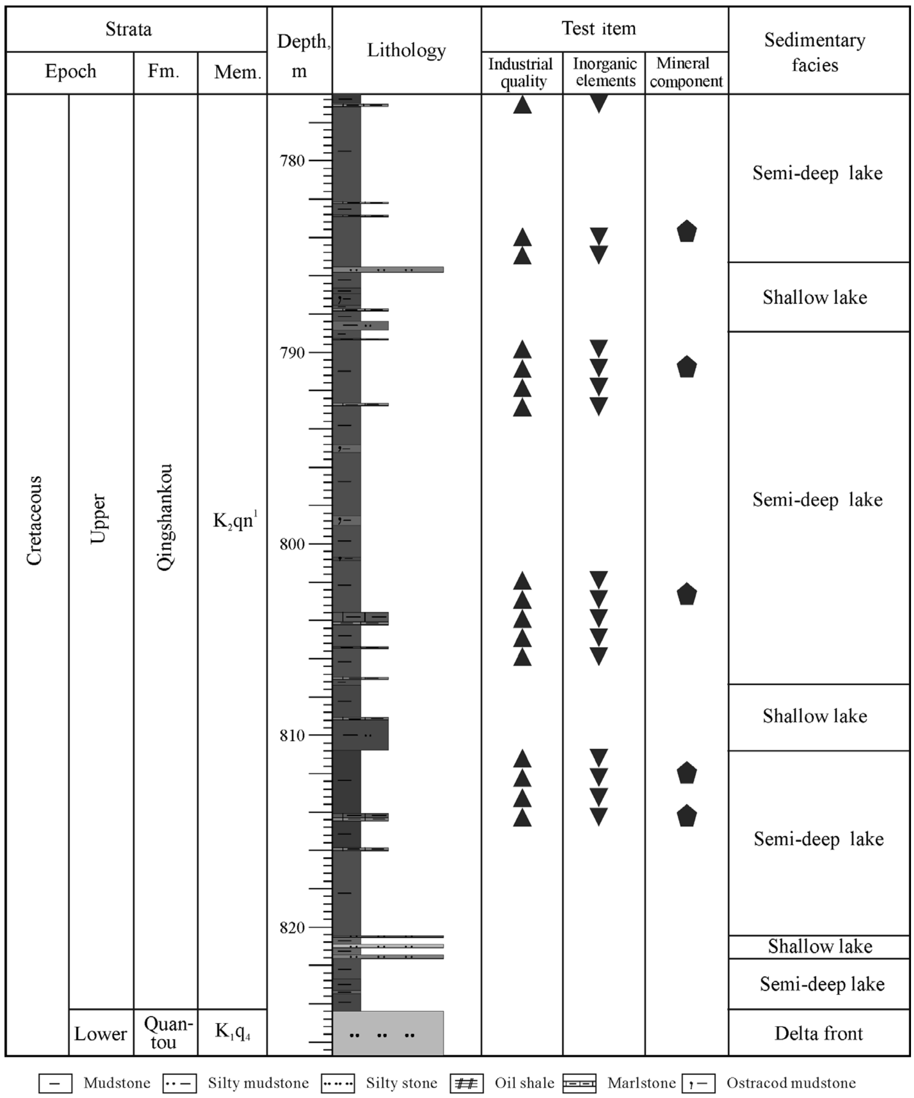

Fig. 3. Lithologic profile with positions of test samples from well ZS3. (The abbreviation used: Fm. – Formation; Mem. – Member.)

4. Petrological and mineralogical characteristics of oil shale

4.1. Petrological characteristics

At present it is universally recognized that oil shale rock types are mainly mud shales, muddy limestones and carbonate rocks [21]. According to the core observations, the K_2qn^1 oil shale in the southern Songliao Basin belongs to mud shales, is mostly of grey-black (Fig. 4a) or dark grey (Fig. 4b) color and with developed horizontal bedding (Fig. 4a), often containing shell sections, Conchostraca and Ostracoda fossils, and pyrite. The sedimentary environment represents a stable reducing semi-deep to deep lake.

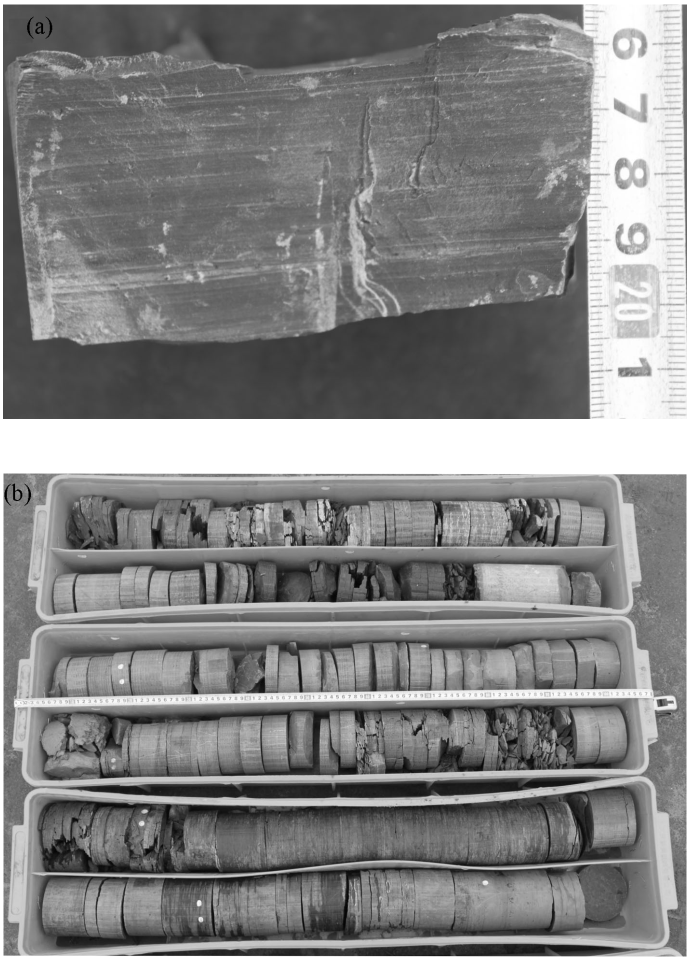

Fig. 4. Photographs of oil shale of the southern Songliao Basin: (a) grey-black oil shale with horizontal bedding, well SY9, 191.85 m; (b) dark grey oil shale, well ZS3, 770.6–776.6 m.

4.2. Mineralogical characteristics

Determined by X-ray diffraction qualitative analysis, the K_2qn^1 oil shale in the southern Songliao Basin is mainly composed of terrigenous detrital, clay minerals, and minor carbonates and pyrite. The terrigenous detrital minerals mostly comprise quartz and feldspars with a total average content of 35.7%, quartz accounting for 19.1–27.8% (avg. 23.3%) and feldspars 9.8–15.8% (avg. 12.4%). The clay minerals content of oil shale was higher, ranging between 46.9 and 65.0% (avg. 55.0%). Carbonates mainly include dolomite and calcite; the dolomite content in some oil shale samples was relatively high, up to 14%, and that of calcite relatively low, being 3.9% at most. The pyrite content was between 1.8 and 4.4%, with an average of 3.3% (Table 1).

Table 1. Mineral contents in oil shale from the southern Songliao Basin

Sample No.	Quartz	Feldspars	Calcite	Dolomite	Pyrite	Clay minerals
SY9-1	21.6	10.2	2.5	6.1	4.3	55.3
SY9-2	26.0	15.8	0	0	4.3	53.9
SY9-3	22.5	9.8	3.9	14.0	2.9	46.9
ZS3-1	25.6	12.8	0	0	4.4	57.2
ZS3-3	27.8	14.2	0	0	4.1	53.9
ZS3-8	19.1	12.6	0	11.8	2.8	53.7
ZS3-12	21.7	11.4	0	0	1.9	65.0
ZS3-15	21.8	11.8	3.0	7.4	1.8	54.2
Average	23.3	12.4	1.2	4.9	3.3	55.0

5. Geochemical characteristics of oil shale

5.1. Chemical composition

Based on the results of studies of chemical composition, the K_2qn^1 oil shale is characterized by a high Si-Al content, low loss on ignition (LOI) and small amounts of CaO, MgO and K_2O. The content of SiO_2 was between 42.1 and 56.72%, with an average of 51.58%, and besides quartz, SiO_2 may also originate from feldspars and clay minerals. The content of Al_2O_3 varied between 12.19 and 16.97%, with an average of 15.02%. LOI made up 9.24–30.22% of the total content, with an average of 16.3%. The contents of CaO, MgO and K_2O were from 1.19 to 10.15% (avg. 3.18%), between 1.74 and 2.69 % (avg. 2.27%), and from 1.74 to 2.69% (avg. 3.40%), respectively (Table 2). Generally, the higher the LOI content, the higher the organic matter content, and, the higher the SiO_2 content, the lower the organic matter content.

Table 2. Contents of major elements in oil shale from the southern Songliao Basin

Sample No.	SiO_2	Al_2O_3	TFe	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	MnO	LOI	Other
SY9-1	44.15	12.85	4.29	1.59	1.74	2.79	1.43	0.45	0.22	0.04	30.22	0.23
SY9-2	55.95	15.79	5.24	1.19	2.16	3.64	1.76	0.53	0.36	0.04	12.99	0.35
SY9-3	49.42	13.83	4.86	2.87	1.98	3.07	1.58	0.49	0.48	0.06	21.18	0.18
ZS3-1	42.1	12.19	5.5	10.15	2.58	2.54	1.4	0.42	0.32	0.07	22.42	0.31
ZS3-3	54.07	16.22	6.05	3.43	2.35	3.81	1.99	0.58	0.34	0.07	10.82	0.27
ZS3-8	56.72	16.97	5.6	1.53	2.69	4.04	2.04	0.61	0.34	0.06	9.24	0.16
ZS3-12	55.38	15.94	5.21	2.73	2.12	3.51	1.8	0.56	0.51	0.04	11.85	0.36
ZS3-15	54.86	16.39	5.91	1.98	2.54	3.79	1.75	0.57	0.32	0.04	11.67	0.18
Average	51.58	15.02	5.33	3.18	2.27	3.40	1.72	0.53	0.36	0.05	16.30	0.26

5.2. Trace elements

Oil shale is often rich in heavy metals. More than 26 trace elements, including Ba, Cd, Co, Cr, Cs, Cu, Ga, Hf, Li, Mn, Mo and U, were identified in the oil shale of K_2qn^1 in the study area and their concentration coefficients were calculated. The concentration coefficient means the ratio of trace elements in the samples to the average contents of geological trace elements in shale and clay rocks. Generally, the greater the concentration coefficient, the higher the concentration of trace elements [43].

The test results showed Mo, U and Pb to be most abundant (Fig. 5) with the highest contents of 17.7, 11.1 and 38.3 μg/g, respectively, and the corresponding concentration coefficients were 4.70, 2.09 and 1.54, indicating that the contents of these elements in oil shale were several times higher than those in shale and clay rocks. Additionally, the concentration coefficients of some elements were found to be higher than one: Sc (1.21), Zn (1.34), Cd (1.23) and Th (1.19) (Table 3). Other trace elements had different degrees of depletion (Fig. 5). The presence of trace elements in the oil shale in the study area suggests mineralization during deposition.

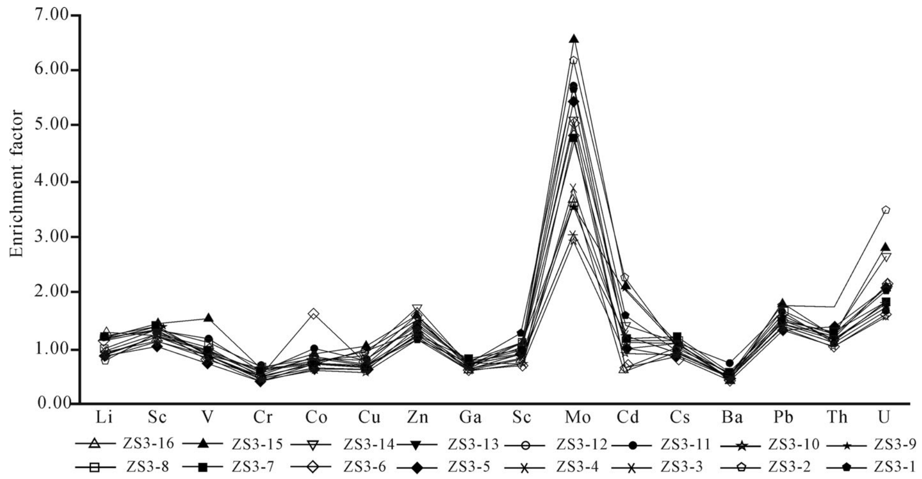

Fig. 5. Trace elements enrichment characteristics of oil shale of the southern Songliao Basin.

5.3. Rare earth elements

Altogether 14 rare earth elements, including Ce, Dy, Er, Eu, and Yb, were identified in the oil shale in the study area (Table 4). Based on the test results, the geochemistry parameters of REEs were calculated and compared with those of North American Shale.

Table 3. Trace elements content in oil shale from the southern Songliao Basin

Sample No.	Trace elements test value, µg/g															
	Li	Sc	V	Cr	Co	Cu	Zn	Ga	Sr	Mo	Cd	Cs	Ba	Pb	Th	U
ZS3-16	54.1	11.3	104	44.5	12.9	34.5	94.2	20.2	315	7.4	0.179	11.5	330	26.8	12.0	6.93
ZS3-15	70.2	14.5	200	63.5	18.3	57.9	120.0	23.7	453	13.2	0.626	12.8	367	36.1	13.1	9.10
ZS3-14	54.9	12.6	126	51.1	13.8	49.7	140.0	22.2	497	10.2	0.423	13.2	416	30.3	13.0	8.46
ZS3-13	75.6	13.9	118	59.6	14.6	36.2	114.0	24.1	437	9.5	0.344	14.4	412	28.7	14.1	5.83
ZS3-12	63.0	11.8	124	48.9	15.2	36.0	95.3	20.5	360	10.8	0.266	12.2	400	28.4	12.5	5.12
ZS3-11	72.7	13.4	152	56.9	20.1	44.2	112.0	22.3	402	11.4	0.303	13.4	584	32.2	13.1	5.35
ZS3-10	77.8	12.2	116	51.6	16.9	36.7	98.3	20.7	343	6.2	0.211	12.2	354	27.8	13.0	7.17
ZS3-9	52.3	14.0	117	55.2	14.5	56.6	125.0	20.5	360	7.1	0.622	12.2	340	32.8	12.1	5.62
ZS3-8	60.3	13.4	143	66.1	16.2	45.9	113.0	22.4	453	7.2	0.341	13.6	408	33.9	13.7	6.73
ZS3-7	53.1	11.6	124	43.5	14.7	38.9	97.7	20.3	572	11.5	0.474	11.6	449	28.2	13.5	6.54
ZS3-6	65.9	13.4	101	46.8	32.9	41.4	132.0	20.9	497	10.1	0.195	12.5	425	30.1	12.3	6.81
ZS3-5	52.1	10.4	88.3	42.7	12.5	33.7	115.0	18.8	349	7.8	0.316	10.4	387	26.7	15.2	6.68
ZS3-4	50.7	11.4	123	43.9	12.7	32.6	94.5	18.5	354	5.9	0.274	10.8	401	27.7	11.4	5.00
ZS3-3	53.3	12.3	113	46.4	12.8	34.9	105.0	19.0	374	6.2	0.368	11.0	414	28.8	12.1	5.94
ZS3-2	47.2	12.7	130	48.1	14.8	53.4	105.0	21.0	497	12.4	0.685	11.8	429	35.4	19.2	11.10
ZS3-1	56.7	12.6	124	55.4	16.5	38.9	121.0	22.2	321	7.8	0.331	13.1	430	28.8	12.8	5.71
SY9-1	36.6	9.9	100	34.0	14.2	46.5	73.4	15.3	316	17.7	0.348	8.9	382	32.5	12.3	6.62
SY9-2	45.2	10.5	106	36.6	14.6	53.0	95.9	16.4	280	6.5	0.293	10.2	482	38.3	10.5	5.10
SY9-3	36.4	8.7	131	36.7	12.4	49.9	77.9	14.9	349	9.5	0.439	8.1	476	30.0	11.8	7.18
Average	56.7	12.1	123.2	49.0	15.8	43.2	106.8	20.2	396	9.4	0.37	11.8	415.1	30.7	13.0	6.68
NASC	60	10	130	100	20	57	80	30	450	2	0.3	12	800	20	11	3.2
Enrichment factor	0.95	1.21	0.95	0.49	0.79	0.76	1.34	0.67	0.88	4.70	1.23	0.98	0.52	1.54	1.19	2.09

Table 4. Rare earth elements content in oil shale from the southern Songliao Basin

Sample No.	Rare earth elements test value, µg/g														∑REE	∑LREE	∑HREE	∑LREE/ ∑HREE
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
ZS3-16	42.70	83.80	9.84	38.10	6.77	1.27	5.73	0.96	5.17	0.89	2.94	0.50	2.56	0.46	201.69	182.48	19.21	9.50
ZS3-15	48.10	96.20	11.00	41.80	7.51	1.46	6.64	1.06	5.36	1.10	3.22	0.49	3.42	0.52	227.88	206.07	21.81	9.45
ZS3-14	43.50	85.00	10.10	38.90	7.16	1.25	5.85	1.05	5.13	1.04	2.60	0.51	2.73	0.47	205.29	185.91	19.38	9.59
ZS3-13	46.10	84.80	10.20	39.00	7.00	1.18	5.57	1.03	5.38	0.99	2.50	0.52	2.91	0.53	207.70	188.28	19.42	9.70
ZS3-12	39.10	78.20	8.94	34.50	6.06	1.07	4.97	0.85	4.76	1.01	2.81	0.40	2.50	0.45	185.62	167.87	17.75	9.46
ZS3-11	43.50	83.20	9.55	36.20	6.34	1.15	5.09	0.92	5.28	1.01	2.49	0.46	2.65	0.48	198.32	179.94	18.38	9.79
ZS3-10	46.50	91.30	10.70	41.20	7.23	1.31	5.46	1.04	5.17	1.04	2.77	0.44	2.72	0.49	217.37	198.24	19.13	10.36
ZS3-9	37.20	72.90	8.29	31.70	5.57	0.96	4.85	0.75	4.13	0.93	2.48	0.37	2.43	0.41	172.96	156.62	16.34	9.58
ZS3-8	44.80	90.00	9.83	38.30	6.68	1.22	5.80	0.98	5.16	1.08	2.74	0.44	2.64	0.45	210.12	190.83	19.29	9.89
ZS3-7	33.90	79.00	8.16	31.90	5.87	1.14	5.00	0.92	5.24	1.02	2.88	0.55	2.97	0.49	179.04	159.97	19.07	8.39
ZS3-6	41.20	82.80	10.10	39.80	7.19	1.32	6.00	0.98	4.90	0.93	2.54	0.36	2.58	0.42	201.12	182.41	18.71	9.75
ZS3-5	42.50	97.10	10.80	42.40	7.96	1.39	5.82	1.24	5.88	1.00	2.98	0.48	2.83	0.42	222.80	202.15	20.65	9.79
ZS3-4	35.20	69.30	8.09	31.60	5.59	1.04	4.90	0.74	4.21	0.86	2.43	0.41	2.18	0.40	166.95	150.82	16.13	9.35
ZS3-3	38.90	78.50	9.19	35.10	6.30	1.22	4.95	0.83	5.14	1.06	2.67	0.44	3.08	0.48	187.86	169.21	18.65	9.07
ZS3-2	48.00	123.00	12.20	48.10	8.96	1.74	7.80	1.32	7.75	1.41	4.23	0.65	3.94	0.63	269.74	242.00	27.74	8.73
ZS3-1	39.00	71.90	8.78	33.30	5.80	1.08	4.88	0.82	4.58	0.91	2.63	0.41	2.67	0.40	177.16	159.86	17.30	9.24
SY9-1	27.00	59.50	6.27	24.20	4.47	0.83	3.51	0.67	4.18	0.82	2.29	0.40	2.06	0.40	136.59	122.27	14.32	8.54
SY9-2	33.30	74.90	7.45	28.70	5.03	0.91	3.73	0.74	3.76	0.82	1.98	0.37	2.42	0.35	164.46	150.29	14.17	10.61
SY9-3	33.90	81.70	7.93	30.70	5.56	1.14	4.73	0.91	4.67	0.98	2.63	0.38	2.30	0.39	177.93	160.93	17.00	9.46
Average	40.23	83.32	9.34	36.08	6.48	1.19	5.33	0.94	5.04	0.99	2.73	0.45	2.72	0.45	195.29	176.64	18.65	9.49
NASC	32.00	73.00	7.90	33.00	5.70	1.24	5.21	0.85	5.80	1.04	3.40	0.50	3.10	0.48	173.22	152.84	20.38	7.50
Chondrite	0.24	0.61	0.10	0.47	0.15	0.06	0.21	0.04	0.25	0.06	0.17	0.03	0.17	0.03	2.59	1.63	0.96	1.70

Being mostly light rare earth elements (LREEs), La, Ce, Pr, Nd, Sm, Gd and Tb were mainly found to be concentrated in the K_2qn^1 oil shale, with average values of 40.23, 83.32, 9.34, 36.08, 6.48, 5.33 and 0.94, respectively, these figures being obviously higher than those of North American Shale. At the same time, the average values of other REEs in the K_2qn^1 oil shale were lower than in the North American Shale. The average value of total REE (∑REE) was 195.29×10^{-6}, being higher than the respective figure of North American Shale (173.22×10^{-6}). The total value of LREE (∑LREE) ranged from 122.27×10^{-6} to 242.00×10^{-6} and averaged 176.64×10^{-6}, which accounted for 90.4% of ∑REE, and was higher than the average ∑LREE of North American Shale (152.84×10^{-6}). However, the total value of heavy rare earth elements (∑HREE) was between 14.17×10^{-6} and 27.74×10^{-6} and averaged 18.65×10^{-6}, being lower than the average ∑HREE of North American Shale (20.38×10^{-6}). The ∑LREE/∑HREE ratio varied between 8.54 and 10.61 (avg. 9.49), which shows that LREEs are relatively abundant in oil shale and their content changes could determine the change of ∑REE.

The chondrite-normalized patterns of the oil shale curve show a distribution trend with a certain slope to the right, and the curves of LREEs are distinctly sloping compared with those of HREEs (Fig. 6a). The NASC-normalized patterns of oil shale show a distribution trend with curves of most LREEs greater than one and those of most HREEs less than one (Fig. 6b). This is consistent with the LREEs enrichment and HREEs deficit described above, while abundant LREEs have some extraction and purification potential.

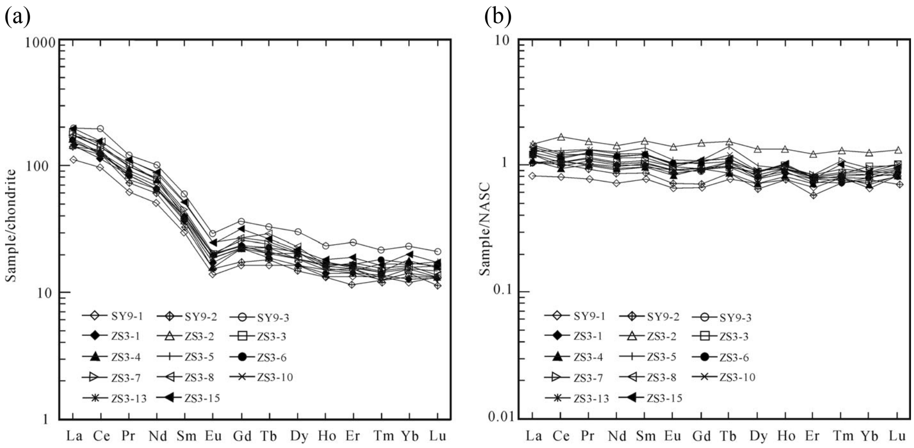

Fig. 6. Rare earth elements patterns for oil shale of the southern Songliao Basin: (a) chondrite-normalized pattern; (b) NASC-normalized pattern.

6. Industrial quality characteristics

6.1. Oil yield

Oil yield (ω) generally refers to the mass fraction of shale oil to oil shale and is the index for oil shale resources categorization. It is also an important parameter for evaluating oil shale's suitability for refining and identifying its quality during low temperature retorting [21]. The cut-off grade of oil yield is 3.5%; above that oil yield can be divided into low-, medium- and high-grade oil yield as follows: $3.5\% < \omega \leq 5\%$, $5\% < \omega \leq 10\%$ and $\omega > 10\%$. The respective measurements in the southern Songliao Basin (Table 5) showed 1-m mixed K_2qn^1 oil shale samples to have the oil yield of 16.37%, the highest ever measured in the basin to date. Of this, the oil yields of ten samples, which accounted for 53% of all samples, were between 3.5 and 5%, those of eight samples, which made up 42% of the samples, from 5–10%, and the oil yield of one sample, accounting for 5% of all samples, was more than 10%. The overall average oil yield was 5.54%, which is characteristic of medium to high quality oil shale, indicating that the K_2qn^1 oil shale has a potential for refining by pyrolysis.

6.2. Calorific value

Calorific value is the full heat released after the complete combustion of a unit weight of oil shale. It is an important parameter for evaluating the worth of oil shale as industrial fuel [9, 21] and mainly depends on the content and composition of organic matter. At present, an international evaluation standard for evaluating the power generation capacity of oil shale has not been established; however, production practice shows that the Palmer oil shale of Israel and the Luozigou oil shale of China, with calorific values as low as 3,000 J/g, still perform well during combustion in circulating fluidized bed boilers (CFBBs) and are used to generate electricity.

The calorific values of K_2qn^1 oil shale samples were all higher than 2,000 J/g and amounted to 10,174 J/g, averaging 3,264 J/g (Table 5). Samples with the respective values greater than 3,000 J/g accounted for 32%, and samples with the values between 2,000 and 3,000 J/g accounted for 68% of all samples, which indicates that the oil shale of the Songliao Basin generally satisfies the experience values for fluidized-bed combustion for power generation purposes.

6.3. Proximate analysis

Being the basic method for characterizing oil shale and evaluating its quality, proximate analysis mainly involves the determination of water, ash and volatile contents using the testing method described in "Proximate analysis of coal" (GB/T212-2008) [44]. All parameters determined by this analysis provide important information also on the type of oil shale and give reference to appropriate methods of its industrial utilization.

Table 5. Industrial analysis parameters of oil shale from the southern Songliao Basin

Sample No.	Top depth, m	Bottom depth, m	Oil yield, %	Calorific value, J/g	Moisture, %	Ash, %	Volatile, %	Sulfur, %
ZS3-16	767.6	768.6	5.14	2971	4.11	83.14	11.33	0.95
ZS3-15	783.6	784.6	4.63	2657	4.27	84.19	11.01	0.88
ZS3-14	784.6	785.4	3.61	2152	4.61	84.54	10.69	1.20
ZS3-13	789.4	790.4	4.25	2030	6.11	81.65	9.69	0.98
ZS3-12	790.4	791.4	5.38	2752	4.37	83.08	12.04	0.75
ZS3-11	791.4	792.4	4.92	2921	4.47	82.42	12.78	1.06
ZS3-10	792.4	793.4	3.60	2165	5.72	83.67	9.92	0.59
ZS3-9	801.4	802.4	4.05	2152	4.73	83.28	11.04	0.90
ZS3-8	802.4	803.4	6.67	3648	4.28	83.02	11.96	1.32
ZS3-7	803.4	804.4	5.67	3063	5.13	81.53	12.49	1.33
ZS3-6	804.4	805.4	3.64	2504	6.32	81.71	11.64	4.08
ZS3-5	805.4	806.4	6.28	2705	6.46	82.04	10.93	1.56
ZS3-4	811.4	812.4	4.27	2430	5.68	83.33	8.49	1.66
ZS3-3	812.4	813.4	7.34	4537	4.39	83.13	9.76	2.44
ZS3-2	813.4	814.4	3.86	2582	4.74	83.56	11.35	1.52
ZS3-1	814.4	815.4	3.59	2653	5.82	83.22	10.70	1.80
SY9-1	240.3	241.3	6.06	3854	3.83	81.48	13.82	1.58
SY9-2	238.3	239.3	5.93	4059	4.04	81.92	13.84	1.94
SY9-3	237.3	238.3	16.37	10174	3.97	67.57	25.70	1.78
Average			5.54	3264	4.90	82.03	12.06	1.49

High or low moisture content may influence heat absorption because of water evaporation when oil shale burns in the boiler. Generally, the lower the moisture content of oil shale, the more efficient its industrial use. The moisture content of oil shale in the study area was relatively low, ranging from 3.83 to 6.46% with an average of 4.90% (Table 5). The samples with the moisture content lower than 5% accounted for 63% and those with the moisture content higher than 5% made up 37% of all samples.

Ash content refers to the mass of the residue remaining after the complete combustion of a unit mass of oil shale. Ash content is both a key index to differentiate between high carbonaceous shale and coal (ash content less than 40% refers to coal) and a parameter to determine the quality of oil shale. The lower the ash content, the higher the content of organic matter, and the better the quality of oil shale. Generally, oil shale with the ash content between 66 and 83% belongs to high-ash oil shales [21, 43, 45]. On the one hand, high ash content causes trouble in the oil shale industry, on the other hand, it is a measure of the quality of building materials. The ash content of K_2qn^1 oil shale was mainly between 80 and 85%, with an average of 82.03%, while samples with the ash content lower than 83% accounted for 42% and those with the ash content higher than 83% constituted 58% of all samples. Therefore, the K_2qn^1oil shale belongs to high-ash oil shales (Table 5).

Volatile content is the amount of gaseous substances emitted by organic matter decomposition under conditions of high temperature and air isolation. It is an important indicator for the evaluation of the quality of oil shale. Generally, the higher the volatile content, the better the quality of oil shale. The volatile content of the K_2qn^1 oil shale was between 8.49 and 25.70% (avg. 12.06%), mostly between 10 and 15% (Table 5).

6.4. Total sulfur content

Total sulfur content (S_Q^g) is the total content of all types of sulfur in oil shale and it is an important index to evaluate the potential environmental pollution from oil shale utilization. During oil shale low temperature retorting or combustion, a harmful air pollutant, SO_2, is released. Generally, the sulfur content could predict the degree of potential pollution: the higher the sulfur content, the heavier the environmental pollution during oil shale utilization. There are distinguished five sulfur content levels of oil shale (S_Q^g): very low ($S_Q^g \leq 1.0\%$), low ($1.0\% < S_Q^g \leq 1.5\%$), medium ($1.5\% < S_Q^g \leq 2.5\%$), high ($2.5\% < S_Q^g \leq 4.5\%$) and very high ($S_Q^g > 4.0\%$) [21]. Our test results showed that the sulfur content of oil shale in the study area was between 0.59 and 4.08%, with an average of 1.49% (Table 5). The samples with S_Q^g lower than or equal to 1.0% accounted for 32%, and those with S_Q^g from 1.0 to 1.5% and higher than 1.5% made up respectively 21 and 47% of all samples. So, the K_2qn^1 oil shale belongs to low-sulfur oil shales.

7. Analysis of oil shale comprehensive utilization potential

Large amounts of ash are produced during oil shale combustion, which, unless used, not only wastes resources, but also causes serious environmental pollution and eventually may become an obstacle to oil shale industry development in general. Therefore, more and more attention is currently being paid to ash utilization, making the maximum possible use of its values. Oil shale ash can be used for the production of building materials, extraction of chemical compounds and metals, as well as production of molecular sieves and adsorbents, etc. [15, 16, 21, 46].

7.1. Extraction of alumina and silica

Oil shale ash is rich in SiO_2 and Al_2O_3 and that is why extraction of these compounds from the ash has aroused wide interest among scholars. When the mass fraction of $A1_2O_3$ in oil shale ash amounts to 20%, pure $A1_2O_3$ can be extracted. Although there is no established complete production line to extract Al_2O_3 from oil shale ash as yet, several scholars have successfully extracted the compound in experiments. By this, Liu et al. [47] and An et al. [48] attained the purity of extracted Al_2O_3 as high as 99.4%. Additionally, Ji et al. [24] prepared superfine γ-Al_2O_3 of 50–80 nm by utilizing oil shale ash. Having advantages such as cheap raw materials, simple preparation and low production costs, the above methods are suitable to be used for the industrial production of Al_2O_3.

Not all forms of SiO_2 can be extracted from oil shale during extraction, only activated silica is amenable to the process [49]. Therefore, the residual organic matter should be first removed from the ash residue by roasting and then alumina and silica in minerals should be activated by treatment with sodium hydroxide [25]. The traditional method to prepare silica uses sodium silicate, silicon tetrachloride and metasilicic acid as silicon materials; however, except for sodium silicate, the other two materials are very expensive, and the use of oil shale ash as a silicon material not only may greatly reduce the production cost of silica but also contribute to the comprehensive use of oil shale resources [17]. There already exists a technology for silica preparation, namely Gan et al. [50] obtained a patent on the extraction of silica from oil shale ash.

Generally, during the extraction process, first Al_2O_3 is extracted from the residuum by alkali treatment and then SiO_2. Earlier studies have shown that Al_2O_3 and SiO_2 in oil shale ash with contents higher than 60% only can be successfully extracted [48–52]. It can be observed from Table 2 that SiO_2 and Al_2O_3 are the main components in the ash of K_2qn^1 oil shale in the southern Songliao Basin, the maximum content of SiO_2 being 55.95% (avg. 48.65%) and that of Al_2O_3 17.23% (avg. 14.59%). The maximum sum of SiO_2 and Al_2O_3 contents was 73.18% (avg. 63.27%). Thus, the ash of oil shale in the study area is suitable to be used for the extraction of alumina and silica.

7.2. Synthetic marble

The mineral components of oil shale ash are mainly quartz, calcite, feldspars and clay minerals, while SiO_2, Al_2O_3, CaO, Fe_2O_3, and MgO are the major chemical compounds. As all the listed components meet the requirements for inorganic fillers of synthetic marble, oil shale ash can be used for the manufacture of the marble [53]. However, the dark color of oil shale ash, which is due to its high Fe_2O_3 content, does not satisfy the requirements for product appearance. To overcome the problem, a small amount of $CaCO_3$ powder as a base padding and $Al(OH)_3$ as a surface padding are added to oil shale ash. The two beds of organic composites can be used to prepare composite artificial marble, and $CaCO_3$ and $Al(OH)_3$ can also be extracted from oil shale ash. The average contents of Al_2O_3 and CaO_3 in the K_2qn^1 oil shale were very high, 15.02 and 3.18%, respectively, which meets the requirements for surface padding for preparing the synthetic marble. Gan et al. [49] obtained a patent on the preparation of synthetic marble from oil shale ash. In the researchers' work, the ratio of oil shale ash in the production materials ranged from 50 to 70%, indicating its efficient utilization.

7.3. Building materials

In the process of electricity generation using oil shale, the optimum temperature of the circulating fluidized bed combustion (CFBC) is between 850 and 950 °C. When the bed temperature of the semicoke circulating in the fluidized bed is below 800 °C, shale ash with a well-developed pore structure and high activity can be obtained and it is suitable for producing building materials such as cement and haydite [16]. The clay minerals and quartz contained in oil shale can be used to produce cement and haydite. Cement is prepared from limestone, clay and iron mine powder. Being rich in clay minerals whose average content is 55%, the ash of oil shale of the southern Songliao Basin can be used to manufacture cement. Ni et al. [54] proposed a method to prepare low clinker cement using oil shale ash. The method employs the proportion of oil shale ash higher than 60% and that of mixing cement clinker lower than 30%. This successfully realizes the resourceful treatment of ash and reduces environmental pollution. Guo et al. [55] proposed a method for preparation of haydite using oil shale ash, the ratios of raw materials were as follows: oil shale ash 20–95%, coal gangue 3–10%, kaolin 3–40% and quartz 4–30%. The high contents of clay minerals and quartz in the K_2qn^1 oil shale satisfy the requirements for ceramsite preparation.

7.4. Extraction of trace and rare earth elements

Oil shales that contain many metal trace elements have drawn increasing attention in recent times. The most notable are the Permian copper shale of Mansfield in the UK, the lead-zinc-rich Monte shale in Australia, the New Albany shale rich in copper and molybdenum in Indiana in America, and the black shale rich in vanadium ore deposits [56] and the polymetallic black shale rich in nickel and molybdenum in southern China [57]. Metal trace and rare earth elements have been successfully extracted from oil shale by chemical separation, extraction and ion exchange [22, 58]. The K_2qn^1 oil shale of the study area is rich in Mo, U, Pb, Sc, Zn, Cd and Th whose abundances in this oil shale are 2–5 times higher than those in ordinary shale and clay rocks. Moreover, the REEs contents of oil shale in the study area are also high. The average value of ∑REE was 195.29×10^{-6}, and the average ∑LREE 176.64×10^{-6}, which is higher than the 152.84×10^{-6} of North American shale and 108 times higher than the Earth's crust's. Generally, the content of trace and rare earth elements in the shale ash left after combustion for power generation is higher [59], and such ash has thus a potential for trace and rare earth elements extraction, which not only reduces oil shale ash-induced environmental pollution, but also increases the economic benefits from and efficiency of oil shale utilization.

7.5. Other uses

In addition to the extraction of alumina and silica as well as trace and rare earth elements, and the production of ceramics and construction materials, oil shale ash, due to the SiO_2, Al_2O_3 and CaO contained, can also be used for the manufacture of molecular sieves and natural rubber packing, and control of water pollution. Currently, various techniques and methods are used to transform oil shale ash into recoverable resources, to double benefits from oil shale utilization, both economic and environmental [17, 21].

7.6. Comprehensive utilization

Based on oil shale petrological, mineralogical, geochemical and industrial quality characteristics, as well as comprehensive utilization analysis, we obtained a way to make most use of K_2qn^1 oil shale of the southern Songliao Basin (Fig. 7). The oil shale with an average oil yield higher than 5% can be used for shale oil extraction by low temperature retorting, and the produced shale oil can be used directly or re-processed. Moreover, the average calorific value of oil shale, 3,264 J/g, which is higher than the limiting lower calorific value for generating electricity (3,000 J/g), means that the K_2qn^1 oil shale can be combusted in a fluidized bed to produce electricity. The ash remaining from retorting and combustion can be comprehensively used. Due to its appreciable amounts of clay minerals, oil shale ash can be used to produce building materials, such as cement and ceramsite, while the notable abundances of SiO_2, Al_2O_3, CaO and MgO in ash allows extraction of these compounds, as well as manufacture of synthetic marble. Metal elements such as Mo, U and Pb can be extracted from ash rich in trace and rare earth elements. During the process of extraction, first alumina is extracted, then

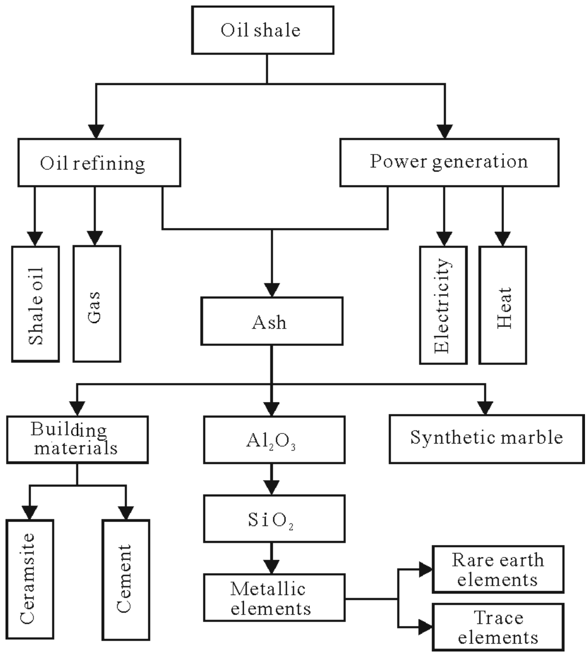

Fig. 7. Comprehensive utilization technological process of oil shale of the southern Songliao Basin.

silica, which results in the accumulation of metal elements in the remaining ash, from which trace and rare earth elements are finally extracted. Overall, in view of its diverse characteristics, the K_2qn^1 oil shale in the study area may be subject to efficient and comprehensive utilization.

8. Conclusions

The study of the characteristics and comprehensive utilization of oil shale in the Upper Cretaceous Qingshankou Formation in the southern Songliao Basin, northeastern China, reached the following conclusions:

1. Oil shale of the Qingshankou Formation in the southern Songliao Basin suitable for industrial use has a medium-to-high oil yield, medium calorific value, high ash yield and low sulfur content. The average oil yield is 5.54%, with a maximum of 16.37%; the average calorific value is 3,264 J/g, with the highest value of 10,174 J/g. The average ash and sulfur contents are 82.03 and 1.49%, respectively. These data demonstrate that the oil shale can be used for refining shale oil, or combusted directly for power generation purposes.
2. The K_2qn^1 oil shale belongs to mud shales and is mainly composed of clay minerals and terrigenous clastic particles, including quartz and feldspars. Oil shale ash with a high content of clay minerals is a good

raw material for producing cement, ceramsite and other building materials.

3. The chemical composition of K_2qn^1 oil shale is characterized by a high content of SiO_2 and Al_2O_3 and a moderate amount of CaO, MgO and K_2O. Oil shale ash that is rich in elements Si, Al and Ca can be used to extract alumina and silica and manufacture synthetic marble.
4. The elements Mo, U and Pb are most abundant in the K_2qn^1 oil shale, their contents in this oil shale being several times higher than those in shale and clay rocks. The rare earth elements La, Ce, Pr, Nd, Sm, Gd and Tb are relatively abundant, their contents being higher than those in North American shale. These data indicate that the oil shale in the study area has a potential for trace and rare earth elements extraction.
5. An economical and efficient scheme of comprehensive utilization of oil shale of the study area has been proposed. It (oil yield $\geq$ 5%) can be directly used to refine shale oil by pyrolysis or combusted in a fluidized bed for electricity production. The remaining ash can be used to produce synthetic marble, building materials (cement and ceramsite), and extract alumina, silica and metal elements.

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