Sedimentary Zeolite Deposits in Iran

Introduction:

Despite the substantial work that has been carried out by many Iranian geologists on exploration and exploitation of different zeolitic deposits in the country, official data and statistics on natural zeolites reserves are very limited and finding any information on zeolite deposits in Iran is very difficult.
It is believed that tens of million tons of natural zeolite resources (mostly sedimentary deposits) are present in Iran and according to the website of National Geoscience Database of Iran (NGDIR), the zeolite formations are scattered in different areas of the country [1,2]. The present brief report is mainly focused on the sedimentary deposits with commercialization potential.

Overview on zeolite deposits:

According to the accessible technical reports (published, unpublished and informal, mostly in Persian), the exploited and operational sedimentary zeolite resources of Iran are mainly situated in Semnan Province and a few in East Azerbaijan Province (see map). Nevertheless, unexploited resources of clinoptilolite with commercial potential are reported in other regions such as Tehran, Yazd, Qom, Kerman, and South Khorasan, etc.

Semnan Province

Semnan (Persian: سمنان) Province, located in the central-northern part of Iran, stretches along the Alborz mountain range and borders the Dasht-e-Kavir desert in its southern parts. Currently, this province is considered as the main hub of zeolite mining, suppliers and distributors in Iran (see Fig. 1).
Three areas of this province (mostly located in NW) have been considered for zeolite exploitation, including, *Vyeen* (Persian: وپين), *Aftar* (Persian: افتر) and *Arvaneh* (Persian: روانه), and *Ab-e-garm* (Persian: آبگرم) [3].

The *Vyeen* region (western, central and eastern), located in the far-west of the province, hosts high quality sedimentary zeolite deposits. Zeolite content and purity of deposits in eastern Vyeen is reported to be of the highest level in this region.

Aftar zeolite resources (35°37'53"N, 53°2'27"E) are situated 32 km NW of Semnan city and 5 km NW of Aftar village, between Aftar and Arvaneh. This deposit is one of the best-studied in the country. Clinoptilolite layers in Eocene tuffs contain more than 600,000 tons of high quality material (85-95% clinoptilolite content). The deposit is in the form of a band extending E-W with outcrop thickness from 15 to 110 m.

Fig. 1 - Zeolite mine (left) and accumulation (right) in Semnan Province [Pictures by K. Azmun].

The geological and mineralogical properties of the Eocene-Oligocene zeolite deposit of *Aftar* region are well-studied. The main zeolite mineral in this area is clinoptilolite and associated minerals in tuffaceous and marly layers are calcite, orthoclase, plagioclase, quartz, clay minerals, biotite and volcanic glass. Based on geological and mineralogical evidence, zeolite formation derived from rhyolitic volcanic eruptions in a shallow sea environment with high pH, which provided suitable conditions for conversion of volcanic glass into zeolites [4].
According to another geological study, zeolite deposits in *Aftar* region are parts of the Karaj formation deposited in the Eocene and composed mainly of light green tuffs and shales. The volcaniclastic materials were precipitated and altered in shallow water south of Alborz mountain range. Deposition of gypsum in this formation confirms the existence of shallow saline-alkaline lake systems. The zeolite minerals are the result of the devitrification of volcanic glasses. The deposited zeolites are classified roughly as grade1 and grade2, with grade1 meaning high purity zeolitic rock, denoted by a white to creamy color. Rocks with low zeolite content are classified as grade2; they have a very light-green to creamy color which is very similar to that the Karaj's green tuffs [5].
Another zeolite deposit located in Sartakht (Persian: سرتخت) (SE of Semnan city) is composed of authigenic zeolite, clay minerals (smectite) and opal-CT. In this deposit, mordenite occurs in minor amounts and commonly coexists with clinoptilolite of lower quality. SEM examination suggests that cliniptilolite is the main constituent, along with scattered mordenite fibers, of the zeolitic tuffs (Fig 2) [6].

A high quality sedimentary zeolite deposit (clinoptilolite) is also exploited in the *Ab-e-Garm* (Persian: آبگرم) region, close to Alaami (Persian: اعلامي) village. This is a volcanic deposit of Eocene age located in the SE of Semnan. The deposit, in which the thickness of zeolite beds is more than 20 meters, is on an anticline, with a gentle dip of 10 to 15°. Clinoptilolite is the main mineral phase of these zeolite-rich tuffs, that also contain quartz, halite and cristobalite.

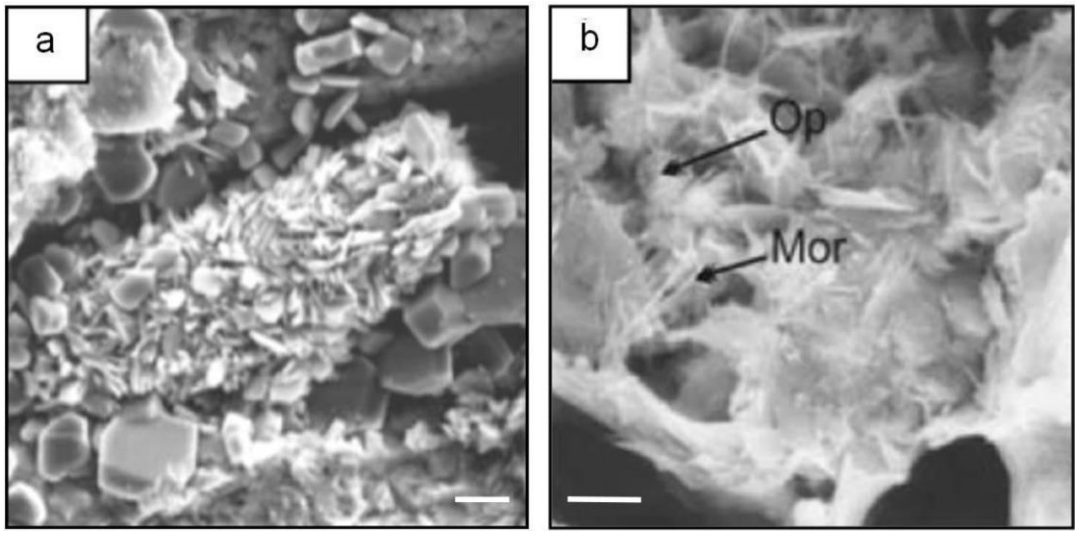

Fig.2 - SEM image of zeolite samples from Sartakht (SE of Semnan) [6]. (a) Ragged and tabular morphology of clinoptilolite crystals; bar = 10 μm. (b)Thin scattered fibers of mordenite associated with opal-CT; bar = 5 μm.

In addition, a zeolite deposit containing clinoptilolite and also bentonite, montmorillonite, cristobalite, quartz and calcite is located in East Dayan-Roba'ee (Persian: لايان رباعي), an area adjacent to the Jandagh Moaleman (Persian: معلمان) and the Damghan main road (Persian: دامغان به جندق), some 100 km south of Damghan with approximate coordinates of 35°24'5"N, 54°8'28"E. The Gandi (Persian: گندی) zeolite deposit, east of the Moaleman, in north-central Iran, is hosted by the Karaj Formation (Middle Eocene), which outcrops from Reshm (Persian: رشم) village to the Gandi zeolite [7].

East Azerbaijan Province

Although Semnan Province hosts most of the active zeolite mines in the country, supplying ~90-95% of the country's market demand for natural zeolite, *East Azerbaijan* Province with a couple of active zeolite mines, is ranked as the second province, supplying ~5-10% of Iran's market demands for natural zeolite (i.e. clinoptilolite). Most of the exploited and mineable zeolite deposits in this province are located in Mianeh County in the vicinity of Mianeh (Meyaneh; Persian: میانه) City, which is situated in a valley, approximately 440 km NW of the Iran capital Tehran and 190 km SE of Tabriz, the largest city of East Azerbaijan. Zeolite deposits of this region are mainly concentrated in Ishligh Chai (Persian: اشلق چاي), 9 km W of Mianeh and N of Shahar-Chai river (Persian: رودخانه شهر چاي). Zeolite deposits are composed of clinoptilolite in andesite tuffs of Eocene age. The zeolite tuffs are overlain by Pliocene conglomerate. Zeolite rocks outcrop in an area of 800 × 800 m^2 with a thickness of 30 m. This clinoptilolite-rich tuff contains quartz, cristobalite, feldspar and montmorillonite as accompanying phases. In addition, several other zeolite deposits (mainly clinoptilolite-rich) have been found in other locations such as Nei Bagh (Persian: نی باغ) (~37°30'N, 48°38'E) and west of Maryam Village (Persian: روستاي مريم) [2]. The chemical composition (wt.%) of a typical natural zeolite rock from the Mianeh deposits is as following: SiO_2 67.35, Al_2O_3 11.73, Fe_2O_3 0.88, TiO_2 0.34, CaO 2.34, MgO 1.21, Na_2O 0.88, K_2O 1.72, LOI 12.94 [8].

Tehran Province

Alborz mountain range is one of the most important geological features in Iran. It is restricted to the Kopeh dagh (Persian: کپه داغ) zone in the north, and central Iranian zone in the south, and is a region of active deformation within the broad Arabian-Eurasia collision zone [9]. The zeolitized green tuff belt of Central Alborz is about 40 km long and is made up of a volcaniclastic sequence of the Karaj Formation of Eocene age. Zeolitization occurred in some beds of Karaj Formation, with a range of 3 to 300 meters in thickness. Based on XRD data, clinoptilolite and smectite are predominant minerals in all altered samples. Paleogeographic conditions indicate a marginal shallow seawater environment, which has been filled by volcaniclastics. In altered tuffs there is a close relationship between clinoptilolite and montmorillonite in some deposits [10]. Some technical and scientific documents report a very high quality natural zeolite resource (i.e. clinoptilolite) in southern part of Froozkooh county (Persian: فیروزکوه). It appears that these deposits are the continuation of zeolite occurrences in the northern Semnan [11].

Qom Province

According to a personal communication (Iraj Navai, 2016), high purity natural clinoptilolite deposits are exploited in this province; however, there are no accessible reports.

Yazd Province

There is a zeolite deposit located in the Erjenan (Persian: ارجنان) region near Ardakan (Persian: اردکان) City in Yazd Province. This is reported as the first and only registered zeolite

mine in the province. This deposit formed as zeolite-rich tuffs in an active volcanic environment under hydrothermal conditions. Geological studies have revealed that this deposit contains a heulandite type zeolite (likely clinoptilolite) with substantial economic potential [12].

South Khorasan Province

According to personal communications from some geologists (Ali Khazaie, 2016), some minable reserves of clinoptilolite-rich tuffs are exploited in this province, however the authors could not find any published and accessible technical report on the claimed resources.

Kerman Province

Deposits of clinoptilolite-rich tuffs with high economic potential have been reported in Ghaleh-Askar (Persian: قلعه عسگر) located in the Baft (Persian: بافت) region [11, 13].

Mineralogy:

No quantitative specific data are available. As reported in the preceding overview, the prevailing zeolite type in every deposit is clinoptilolite and its content ranges usually between 80 and 90%. Associated minerals are also indicated for specific rocks in some described deposits [14].

Chemistry:

Chemical composition

The following table reports the representative composition (main components) of typical clinoptilolite-rich rock samples from the Senman deposits (wt. %). The reported names are those of zeolitic products for export (Zeodigest®) or of registered Iranian companies (Afrand Tooska, Afrazand), marketing zeolitic products for domestic use.

Oxide	Zeodigest	Afrand Tooska	Afrazand
SiO_2	62-67	66.5	68.0-68.5
Al_2O_3	10-12	11.8	10.1-11.5
Fe_2O_3	0.5-1.0	1.3	0.2-2.0
CaO	1-3	3.2	0.6-2.5
K_2O	1-3	3.1	1.4-4.4
Na_2O	1-3	2.0	1.8-4.3
H_2O*	8-10	12.0	10.0-12.2

*Measured on dried commercial samples. There is therefore no specific relationship with zeolite content.

Cation exchange capacity

The cation exchange capacity (CEC), estimated according to the standard ammonium acetate method, ranges between 1.5 and 2.0 mequiv/g (Zeodigest®) and between 1.7 and 2.0 mequiv/g (Afrand Tooska).

Cation exchange selectivity

$Cs^+ > NH_4^+ > Pb^{2+} > K^+ > Na^+ > Cu^{2+} > Zn^{2+} \sim Sr^{2+} \sim Cd^{2+} > Ni^{2+} > Co^{2+}$ [13].

Crystallography:

The unit cell parameters of clinoptilolite from Sartakht (Semnan province) are as follows [6]:

a [Å]	*b* [Å]	*c* [Å]	*β* [°]
17.624	17.906	7.395	116.15

Physical and chemical properties:

The main physical and chemical properties of Zeodigest®, a product from Semnan region for international markets, are summarized in the following box [Zeodigest® technical data sheet, updated 2015).

Appearance (colour)	gray-green
Hardness (Mohs)	3-4
Rock porosity	25-30%
WHC (water holding capacity)*	62-79%
Effective pore diameter	0.4 nm
Surface area (BET)	30-50 m^2/g
Density	2200-2400 g/cm^3
Bulk density (1-3 mm particles)	850-900 g/cm^3
Bulk density (0-1 mm particles)	950-1000 g/cm^3
pH of slurry (zeolite/water 1:10)	~9
Softening temperature	1200-1250°C
Melting point	1300-1350°C

* Measured according to ISO 11267.

Reserves and production: Sedimentary zeolite resources are huge, of the order of tens million tons. The Semnan Province alone hosts more than 16 million tons of proven sedimentary zeolite reserves that have potential for economic exploitation.

Currently more than 10 zeolite mines (mainly clinoptilolite) are registered in Semnan province, in which 3-4 mines are active operational and supply more than 95% of the country's natural zeolites demands, mainly for animal husbandry, aquaculture, agriculture and cement and construction industries [14, 15]. There are several registered Iranian companies that are producing and distributing different natural zeolite products to the domestic markets such as Afrandtooska, Fath-e-Alborz, and Afrazand companies. Most of the production plants are located in Semnan Province, while at least one processing plant is in Karaj Province. Since 2014, at least one Iranian company; has marketed its natural zeolite products (i.e. Zeodigest®) in other countries, in Asia, Africa, Europe and even in North America.

Main applications: Iranian zeolitic products (clinoptilolite) with different brands have been and are being marketed for, but not limited to, the following applications:

(a) Animal feed additive for different livestock mainly in poultry industries. For example, Anzymite® is one of Afrand Toska's products in the domestic market and Zeodigest® is the product that the Zeodigest Company is distributing in international markets.
(b) Aquacultural applications.
(c) Soil remediation and other agricultural applications.
(d) Animal bedding and pet litters.
(e) Construction industries, zeolite-based lightweight concrete products, pozzolan.
(f) Odor adsorbent for household applications.

Concluding remarks Sedimentary zeolite deposits are widespread in different regions of the country. Currently, Semnan Province is the main hub with numerous registered and active zeolite mines and zeolite suppliers. Tehran Province (e.g. Firoozkooh region) is considered as another region with huge potential for extraction of high quality zeolites (clinoptilolite). East Azerbaijan (Meianeh region) is already contributing to the Iran zeolite market with potential for further development.

It is noteworthy that despite the fact that the authors of this report worked tirelessly to put together a comprehensive text by using reliable sources and reports, in order to give a clear picture of Iran's huge potential in this field, this report will have to be revised and updated in the future. The authors will be delighted to hear feedback from others in order to make the report a reliable source of information for researchers and investors in the future.

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