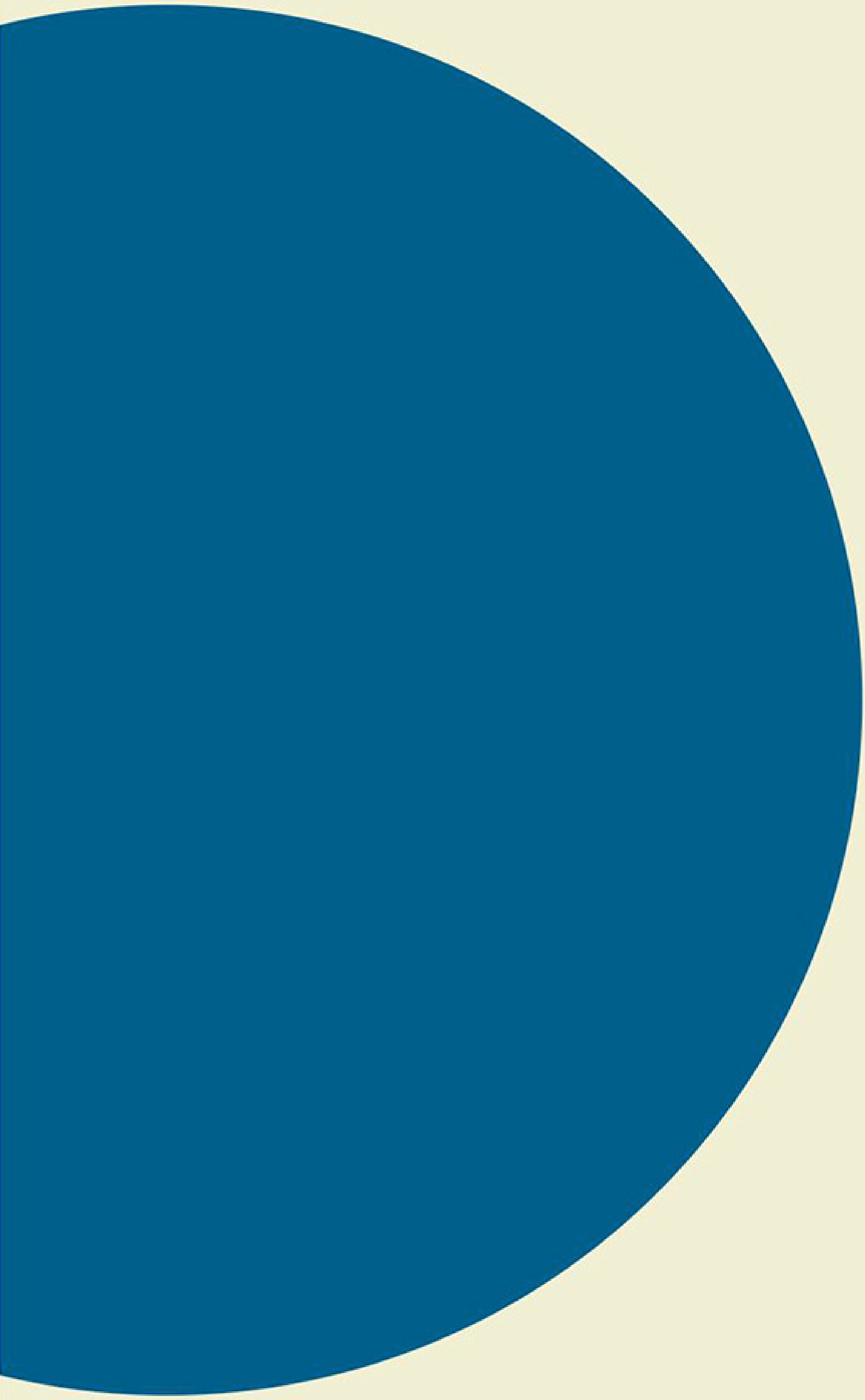
DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2018/8

Raw materials for additives in combustion of wood pellets

Preproject 2018

Christian Knudsen



GEOLOGICAL SURVEY OF DENMARK AND GREENLAND
DANISH MINISTRY OF ENERGY, UTILITIES AND CLIMATE

GEUS

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G E U S

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1 Introduction

This report is a desk study carried out in February and March 2018 by GEUS in cooperation with Bo Sander at Ørsted A/S 2018.

1.1 Objectives:

The objectives of this study are to identify different raw materials that potentially could be used as additives to the fuel (wood pellets) for neutralizing the negative effects of elements such as K and Cl liberated during combustion of the wood. Further, some preliminary considerations concerning the logistics of mobilising the additives to a power plant in Denmark will be touched upon.

The database at GEUS as well as available data about chemical and mineralogical composition of potential additives in Denmark and surrounding countries is summarised. The main focus will be to identify raw-materials with a high content of Al.

1.2 Background

When wood is combusted, a number of ash-forming elements present in the wood such as K and Cl can cause problems with slagging, fouling and corrosion in the boiler. These problems can be abated by blending the fuels with additives into the combustion systems. Such additives can:

- reduce concentrations of problematic ash species (i.e., KCl) in the combustion system by means of physical adsorption.
- bind and convert low-melting species into less troublesome compounds with high melting temperatures;
- enhance ash melting temperatures by altering or diluting the ash composition with refractory elements

At present, this problem is solved by adding coal fly ash to the wood pellets. However, when coal is no longer used as a fuel in Danish power plants in 2020, this material will no longer be available and there will be a need to identify alternative materials for this purpose.

Punjak *et al.* (1989) pointed out that vapors of alkali metal compounds can be removed from combustion and gasification flue gases using high-temperature alumino-silicate sorbents such as kaolinite and bauxite in a complex combination of diffusion and reaction. Aluminium silicates is group of materials that have been tested successfully to abate the slagging, fouling and corrosion problems (Wang *et al.* 2012, Wang *et al.* 2018, Niu *et al.* 2014).

Kaolinite decomposes at temperatures between 450 °C and 600 °C by releasing water and forming an amorphous mixture of alumina and silica called meta-kaolinite. The meta-kaolinite suppresses the release of potassium from the biomass and removes gaseous potassium species by reacting with potassium compounds into potassium aluminum silicates with high melting temperatures ($KAlSiO_4$ (kalsilite) and $KAlSi_2O_6$ (leucite), which have melting temperatures of greater than 1600 °C and 1500 °C, (Niu *et al.* 2016).

The price of refined kaolin is high, and there is a need to identify cheaper alternatives. The key properties for the additive are:

- High reactivity and surface area to facilitate fast reaction in the boiler
- High temperature stability and high melting point itself to minimise the risk of forming a melt that can create slagging and fouling in the boiler.

The focus in this is on clay-rich deposits and similar raw materials. The main concerns are:

- The price of the raw material at the source
- The cost of bringing the additive to the plant
- The content (%) of active minerals in the material
- The effectiveness of the active minerals
- The potential need for processing of the raw material before introducing it in the boiler
- Possible negative effects of other minerals

There are a number of different types of raw materials to consider:

- Danish clay types
- Kaolin-rich deposits from neighbouring countries
- Bauxite
- Restite from aluminium production
- Tailings/overburden from quarrying/mining.

2 Danish clay types

The following is a very brief summary based on my database of compositional data compiled from different tasks over the years.

Danish clay types can roughly be divided in four groups:

- Clay-rich till deposited by the ice during the ice age.
- Clay deposited by water during the ice age.
- Clay deposited in the Tertiary period (65 to 2 million years ago)
- Jurassic clay of the Bagå Formation, Bornholm

The range of chemical compositions of the Danish clay-rich rock-types is illustrated in Figure 1. The range of compositions is a function of the minerals present in the different deposits.

The different sediment-types are characterised by different ratios between $Na_2O + K_2O$ and Al_2O_3 (Figure 1). This ratio is a function of the average composition of the aluminium silicates in the sediment. The higher the content of Al_2O_3 in Figure 1 the higher the content of the Al bearing minerals in the sediment. Compositions with high $Na_2O + K_2O$ are likely to melt at temperatures below 1200°C.

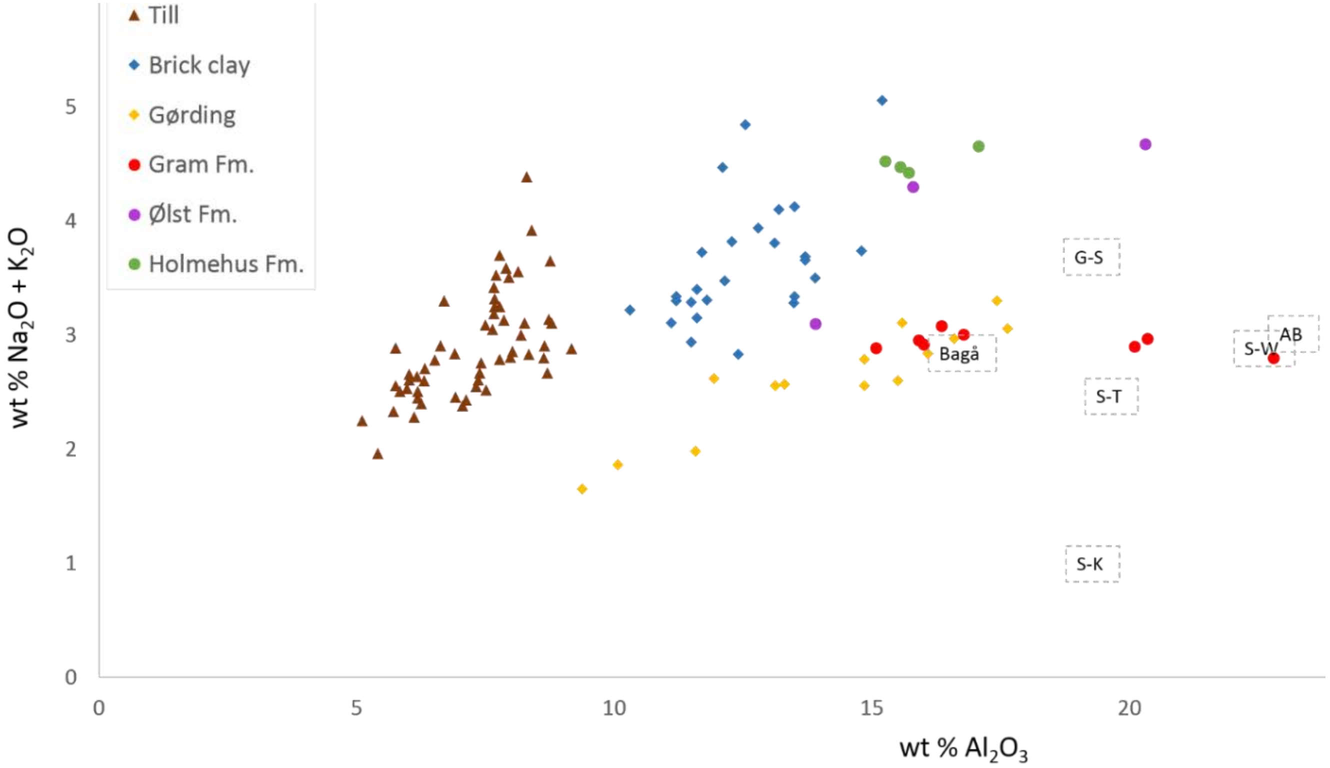


Figure 1 *Content of $Na_2O + K_2O$ versus Al_2O_3 in common clay-types in Denmark (Data from GEUS database) compared to commercially available raw kaolinite-rich clays. Bagå is average Bagå Formation; AB altered basement from Bornholm; S-T: Schmidt Tone; S-K: Sibelco raw kaolinite; S-W: Sibelco Westerwald clay.*

2.1 Clay-rich till

Till is an unsorted, heterogeneous sediment of a glacier. The composition is a mixture of clay, sand, gravel, and boulders. The clay-till is the clay-rich variety deposited from the ice sheet that covered Denmark during the ice age. The till have a high $(Na_2O + K_2O)/Al_2O_3$ ratio (Figure 1) due to a high content of feldspars (characterised by a high $(Na_2O + K_2O)/Al_2O_3$ ratio as compared to clays).

2.2 Clay deposited by meltwater

The clays formed during the ice age were deposited in lakes in the ice-sheet that covered Denmark, and consists of a mixture of clay minerals, quartz, feldspar, mica and carbonate. The grain-size distribution varies and the clay constitute typically between 20 and 40 % of this sediment. Clay deposited during the ice-age form the raw materials for brick production in Denmark, and can be divided into yellow and red burning clay. The difference is the content of calcium carbonate, where the yellow burning clay contain calcium carbonate whereas the carbonates has been leached out in the red-burning clay that form a 1 – 2 m thick cap over yellow burning clay (blå-ler).

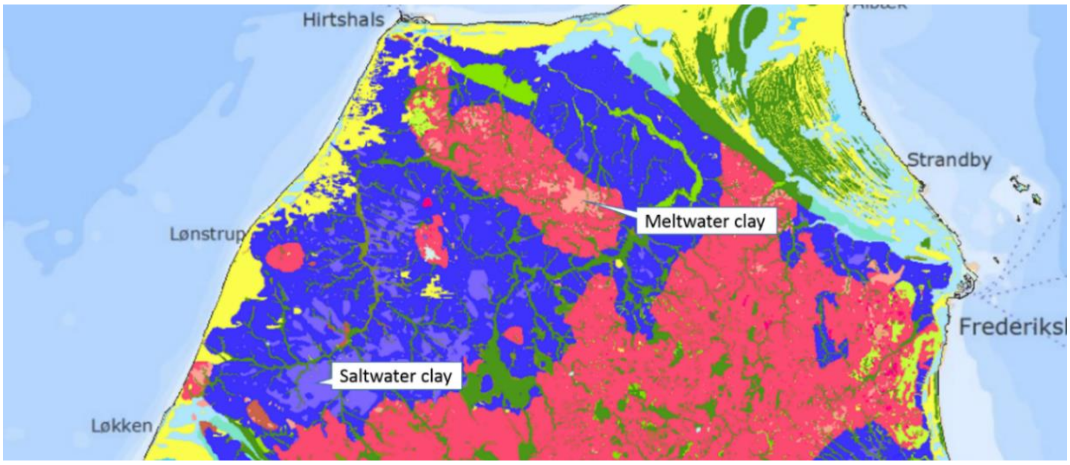


Figure 2 *Geological map showing the distribution of sediment types in Northern Jutland with meltwater clay and saltwater clay highlighted. http://www.geus.dk/DK/data-maps/Sider/j25-dk.aspx.*

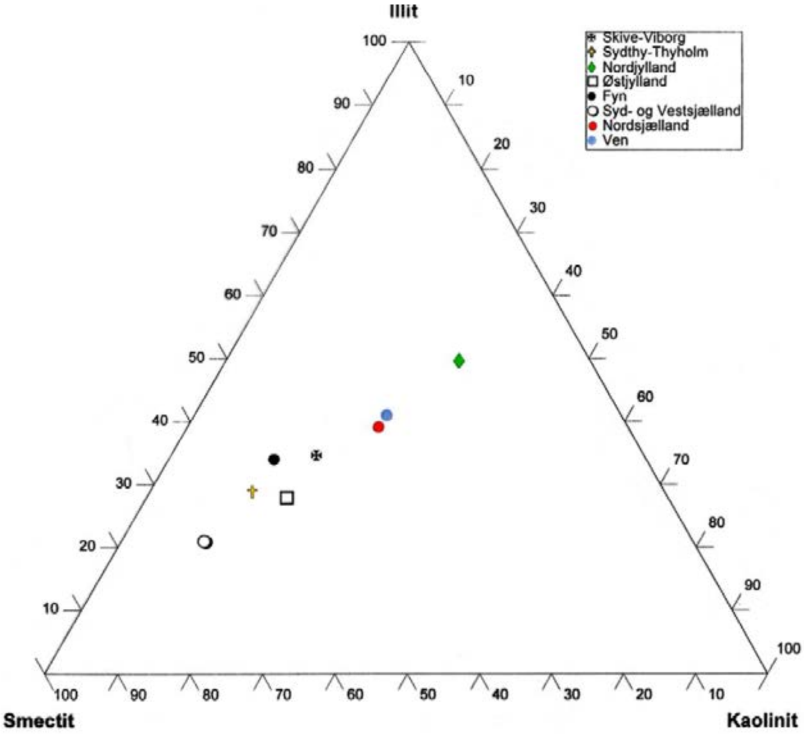


Figure 3

Distribution of clay minerals in meltwater clay in Denmark. Data from Jørgensen (1989), Ditlefsen (1988), Hegel (1992) and Ernstsen (1998).

In Northern Jutland, there are marine clay deposits formed in the sea during the ice age (saltwater clay on Figure 2). These deposits contain NaCl. There is a regional as well as local variation in the distribution of clay minerals related to the provenance (the source) of the clay. The typical clay minerals in the Danish clays are smectite, illite, kaolinite, and the different clay minerals, which account for the variation in the chemical composition shown on Figure 1 and the mineralogical distribution of the clay minerals shown on Figure 3 and 4. In south and western Zealand and eastern Jutland the clay-mineral distribution is influenced by the underlying Tertiary formations one (smectite-rich) whereas the northern Jutland and northern Zealand is dominated by clay from Scandinavia.

All the brick clays mentioned have a common feature which is that the bricks will melt if the temperature goes above 1100°C. Apart from this, the clay content in the normal brick clays mentioned above is low compared to other clays in Denmark and probably not the best candidates for additive in Denmark.

In the Gørding area (south-western Jutland) the clay is redeposited Gram Formation (Figure 1). The brick factory in Gørding is the only place in Denmark where it is possible to make bricks that can be fired to > 1200°C probably due to the low content of alkalis (Figure 1). This clay could be a possible additive, but the resource (amount present) is not likely to sustain the use for additive.

2.3 Clay deposited in the Tertiary period in Denmark

The distribution of the different geological ages in the pre Quaternary (i.e. the formations under the of deposits from the Ice-age) in Denmark is shown on Figure 4 (c. 58 – 10 million years old).

After the deposition of the chalk ceased c. 60 million years ago in Denmark, the sedimentation in the sea that covered Denmark was dominated by smectite-rich clays derived from volcanic ash. Abundant smectite in the Paleocene and early Eocene reflects alteration of volcanic ash derived from pyroclastic activity associated with the opening of the North Atlantic between Greenland and Europe by rifting of the crust. The most prominent expressions of this is the Æbelø Formation, Holmehus Formation of Palaeocene age (*c.* 58 Ma) and the Ølst Formation of early Eocene age (*c.* 55 Ma, Figure 5 & 6).

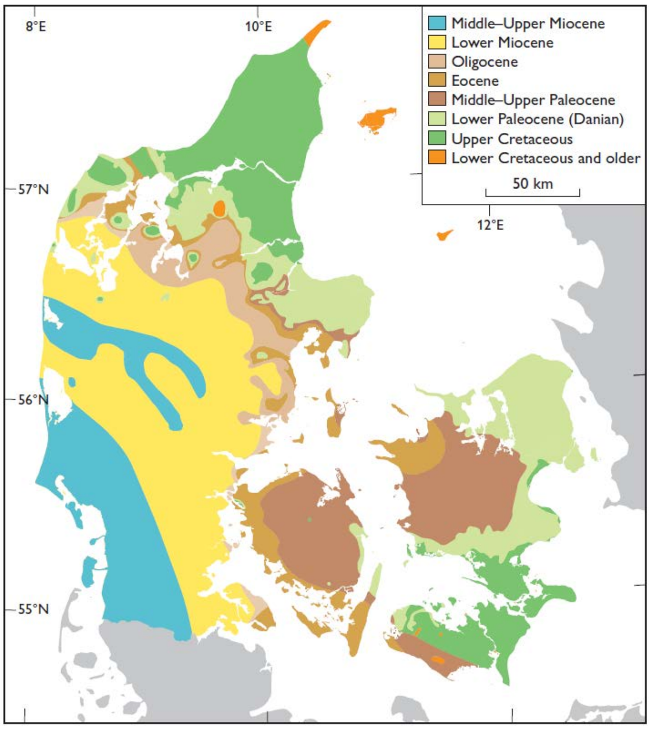
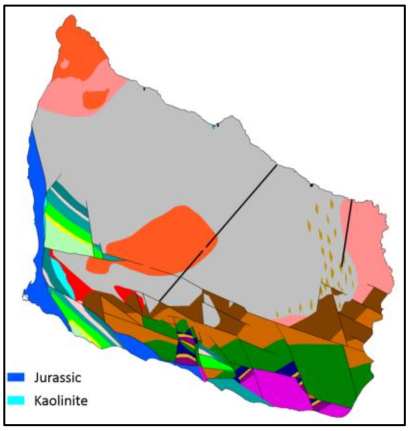


Figure 4

Geological map of Denmark (Knudsen, 1998) and of Bornholm (Varv 1977).



After this period, the influx of volcanic ash decreased and the clay-rich sediments became dominated by influx of weathering products derived from Scandinavia gradually richer in illite and kaolinite (Figure 6) in Oligocene and Miocene time.

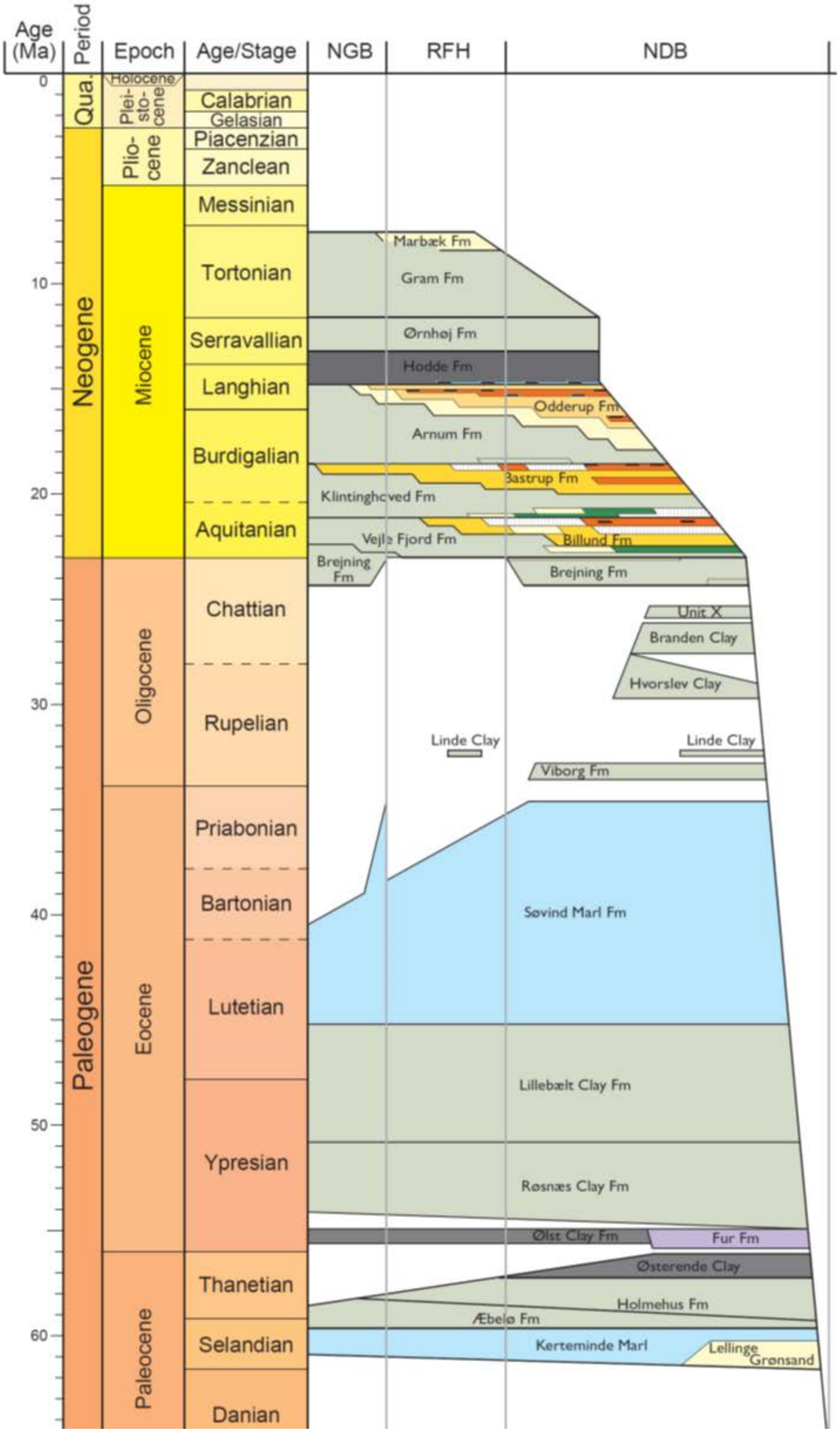


Figure 5 *Stratigraphy of the Tertiary sediments in Denmark from North (right) to South (left). Note that the vertical scale is time and not thickness of the units.*

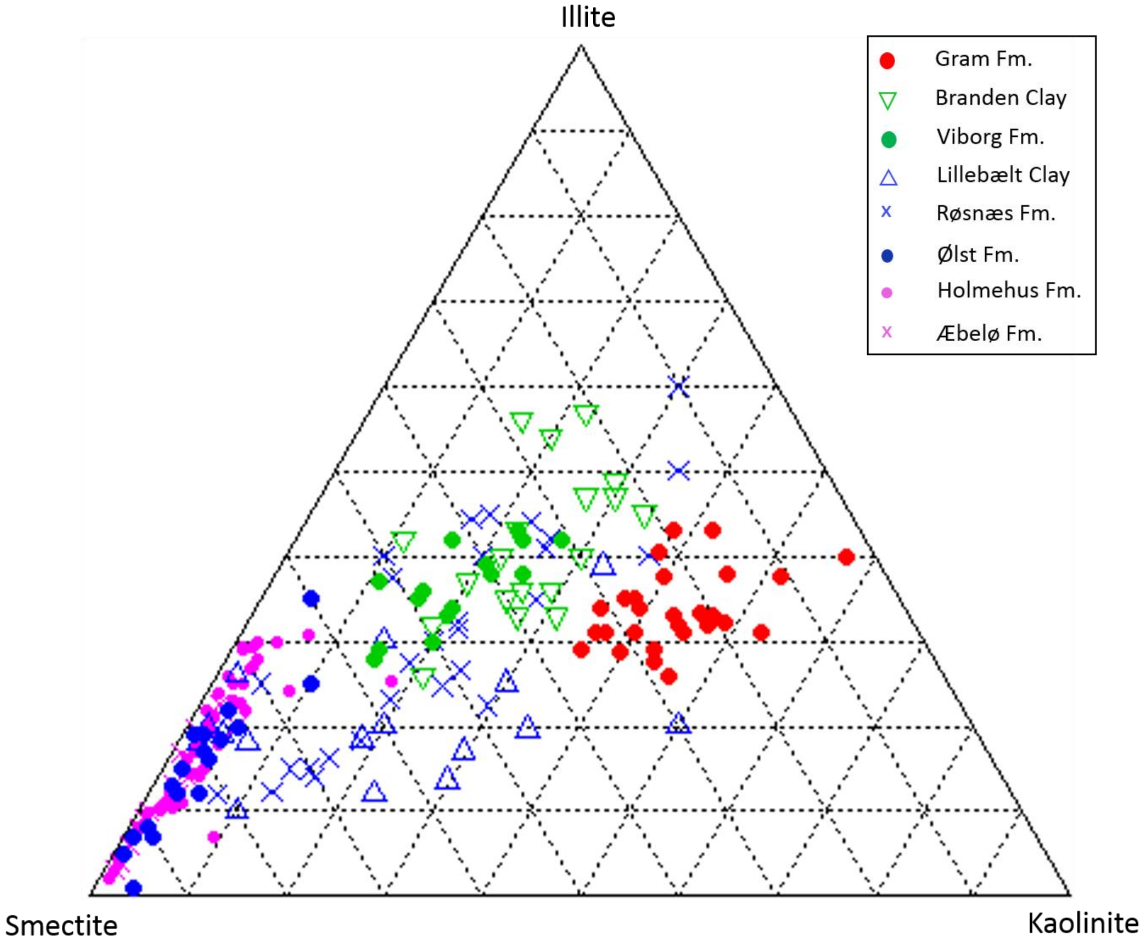


Figure 6 *Distribution of clay minerals in the Tertiary formations in Denmark. Data from Andreassen (1989), Deyu (1987), Friis (1994), Heilmann-Clausen (1984), Heilmann-Clausen (1995), Mikkelsen (1985) and Mikkelsen (1989), Pedersen (1992), Rasmussen & Larsen (1989). Paleocene is pink, Eocene is blue, Oligocene is green and Miocene is red.*

2.3.1 Holmehus Formation

The Holmehus Formation is dominated by smectite (Figure 6) which will be less thermally stabile as compared to kaolinite and will form a melt at the wood combustion temperatures. However, the clay content in this formation is very high, the content of silt and quartz low and the specific surface area is likely to be high relative to other clay-rich formations in Denmark.

Very smectite-rich clay is called bentonite and have the capacity to expand when exposed to water. This ability have a number of industrial applications e.g. in drilling mud and for liners in waste dumps. Over the past 25 years there have been a number of initiatives to start a production of bentonite and there is currently production of bentonite from the Holmehus Formation on Tåsinge by the NCC owned company Dantonit (Figure 7). This imply that it will be logistically simple to get samples from this formation even for full scale tests of this material.

If the bentonite from Tåsinge has properties that make this type of clay relevant as an additive, it is likely that similar occurrences closer to Avedøreværket e.g. on Sjælland or Lolland could be possible targets.

Figure 7 *Quarrying of the Holmehus Formation on Tåsinge. (Picture from http://www.dantonit.dk/).*

2.3.2 Hinge

Since 1939 there have been a production of Lightweight Expanded Clay Aggregate (LECA) in Denmark, in the first many years based on clay from Røsnæs. Now the production is based in Hinge, Eastern Jutland – based on glacially disturbed Palaeocene and Eocene clays belonging to the Holmehus Fm., Ølst Fm., Røsnæs Clay and Lillebælt clay. The deposit is rich in clay and dominated by smectite, but with illite and kaolinite (Figure 6) giving the clay a different bulk composition. The LECA production is based on the ability of the smectite to expand during heating. The clay is fired in rotary kilns at ca. 1150°C and the aggregate is formed.

Figure 8 *Quarrying of the Ølst Formation in Hinge (Picture from http://www.leca.dk/om-leca/produktion/).*

2.3.3 Gram clay

The highest proportion of kaolinite in the clay fraction among the Tertiary Danish clays is found in the Miocene clays of the Gram Formation (Figure 6). The Gram Formation is found under a few meter thick cover of Quaternary in southern and western Jutland. The thickness of the exposed section is ca. 13 m at Gram, where the lower part of the Gram Formation is exposed in the claypit active until 1988. The mineralogy and grain-size distribution of the profile is shown on Figure 9. The formation thickens towards South-west and 105 m was penetrated in the Tinglev borehole. The Gram Formation was deposited in a fully marine environment with water depths of more than 100 m. The Gram Formation consists of dark brown clay, which becomes more silty upwards. Siderite concretions are common in the lower part of the formation, and pyrite is common consisting about 2 % of the sediment (avg. 1,8 wt % S of 27 samples). The formation is also rich in organic material which constitutes *c.* 2 % of the volume (avg. 1,6 % org C of 27 samples, Rasmussen & Larsen, 1989). The best known occurrence is in Gram, where there was a clay pit tied to the now abandoned brick factory and there is access to the clay, kept open in connection with the Gram Museum.

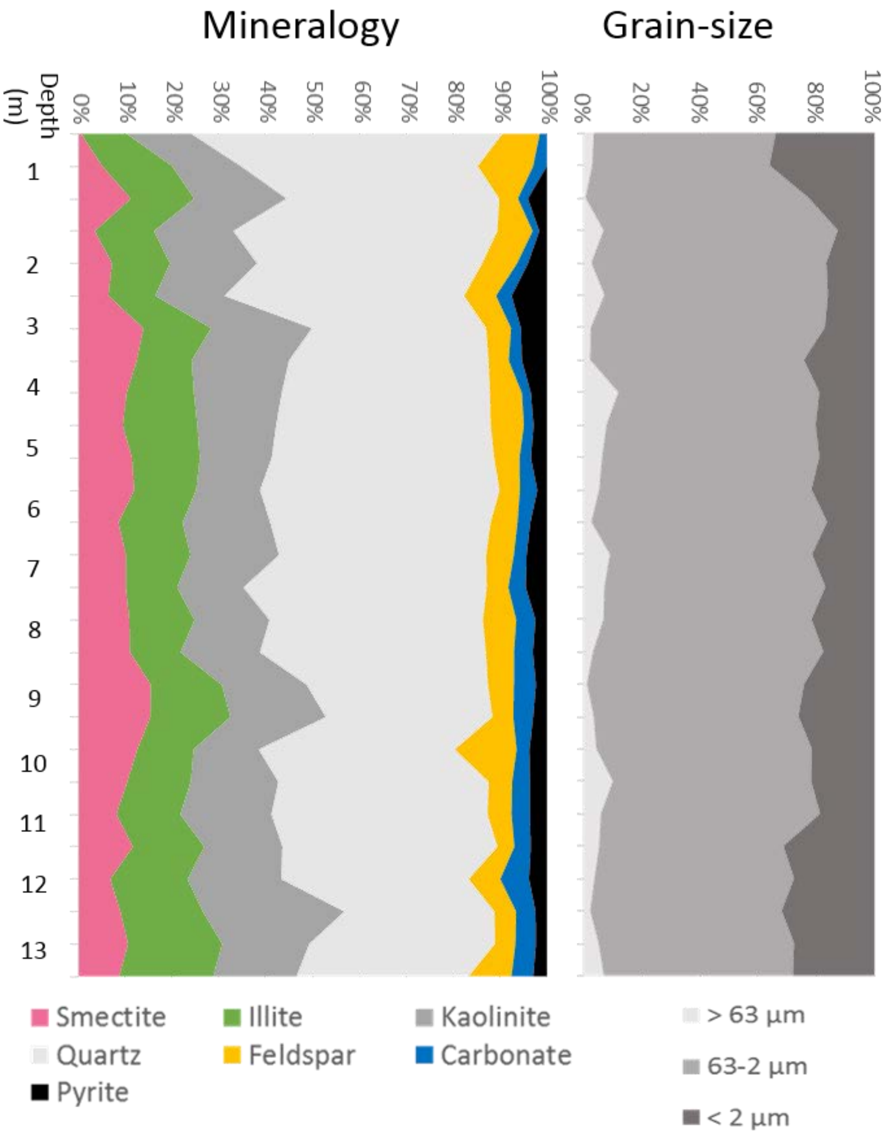


Figure 9 *Mineralogy and grain-size distribution in the Gram clay pit (Rasmussen & Larsen, 1989).*

Figure 10

Gram clay pit in 1981.

The clay had been excavated for more than 100 years when the pit was closed in 1988.

The pit was re-opened again in 1996 for fossil hunters to collect specimens.

2.4 Kaolinite alteration of granitic basement on Bornholm

Kaolinite rich clays have been mined on Bornholm since the late 18th century and has been used for the production of porcelain, filler in paper, and refractory products. The kaolinite is an alteration product of the Rønne Granodiorite where the feldspar has been altered to kaolinite whereas the quartz and mica is still present (Figure 11). The alteration started in the late Triassic and continued in the Jurassic period and the rock now consists of approx. 20 % kaolinite.

Composition of the Rønne granodiorite is shown on Figure 11 together with the alteration products (Bondam 1967). Increasing degree of alteration leads to decrease in the content of alkalis and increasing aluminium.

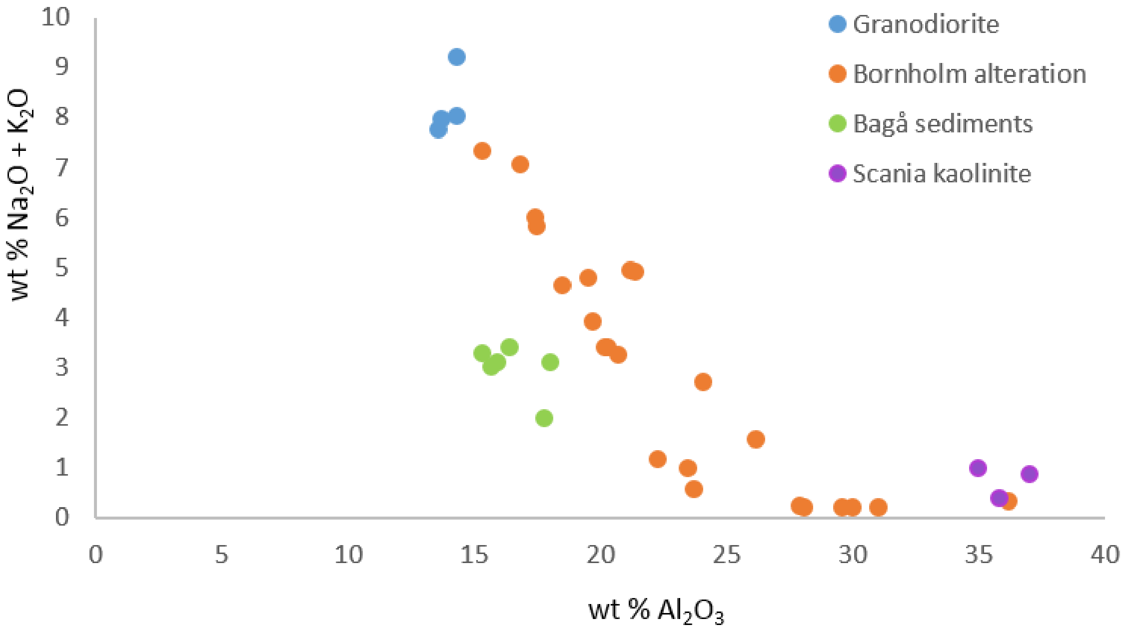


Figure 11 *Composition of the Rønne granodiorite and the kaolinite bearing alteration products (Bondam 1967), clay belonging to the Bagå Formation (Graff-Petersen 1961) and the kaolinite from Scania (Lidmar-Bergström 1997).*

2.5 Kaolinite-rich Jurassic clay on Bornholm

The Jurassic Bagå Formation is found near Hasle on Bornholm (Figure 4 & 12) has been the target for extraction of coal and clay for centuries. Production of tiles and bricks in the area started in the 1860'ties and lasted until 1998, where it stopped for economical reasons. The location of the clay-pit is shown on Figure 12. It is now filled with water.

The stratigraphy in the old clay-pit is shown on Figure 13. The Bagå Formation consists of up to 10 m thick laminated to homogeneous, grey clay units with dark to black coaly clays with rootlets together with up to 2.5 m thick coal beds. Further, the succession contain up to 5.5 m thick medium- to fine-grained, cross-bedded or poorly laminated sand beds (Michelsen *et al.* 2003). The total thickness of the Bagå Formation is ca. 190 m (Gry, 1969). The clay was deposited in rivers, lakes and swamps together with wood that developed to coal with time. The clay was washed into this environment from deeply altered basement to the east together with sand and wood. The clay consist of a mixture of *c.* 20% illite, 45 % kaolinite, 10 % "mixed layer", 20 % vermiculite and 5 % chlorite (Graff-Petersen (1961) and the chemical composition of typical clays is shown on Figure 11 (green dots).

It is considered likely that further clay resources can be located, but the possibilities of getting permission to mine in the area is unknown.

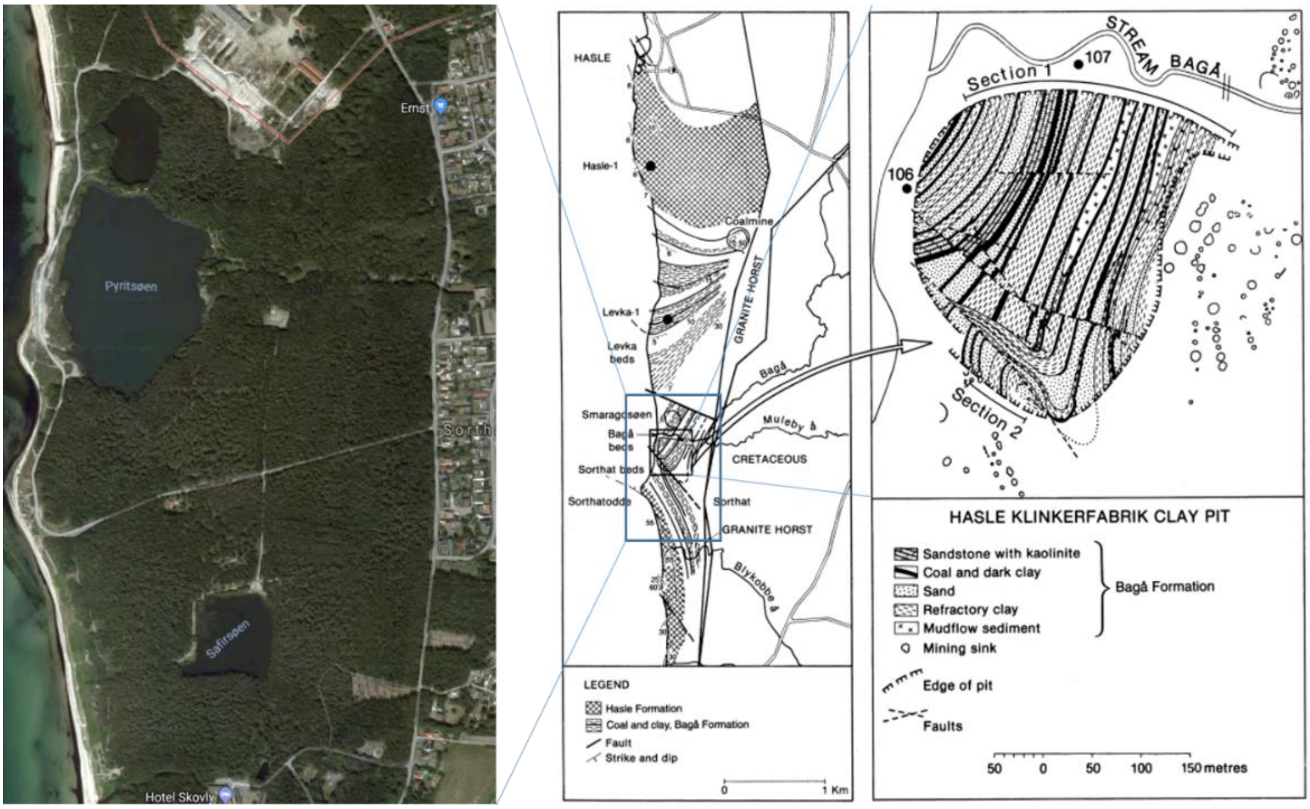


Figure 12 *Map showing the Bagå area with measured Section 1 and 2 indicated (Figure 12). After Gry 1969. The clay pits are now lakes.*

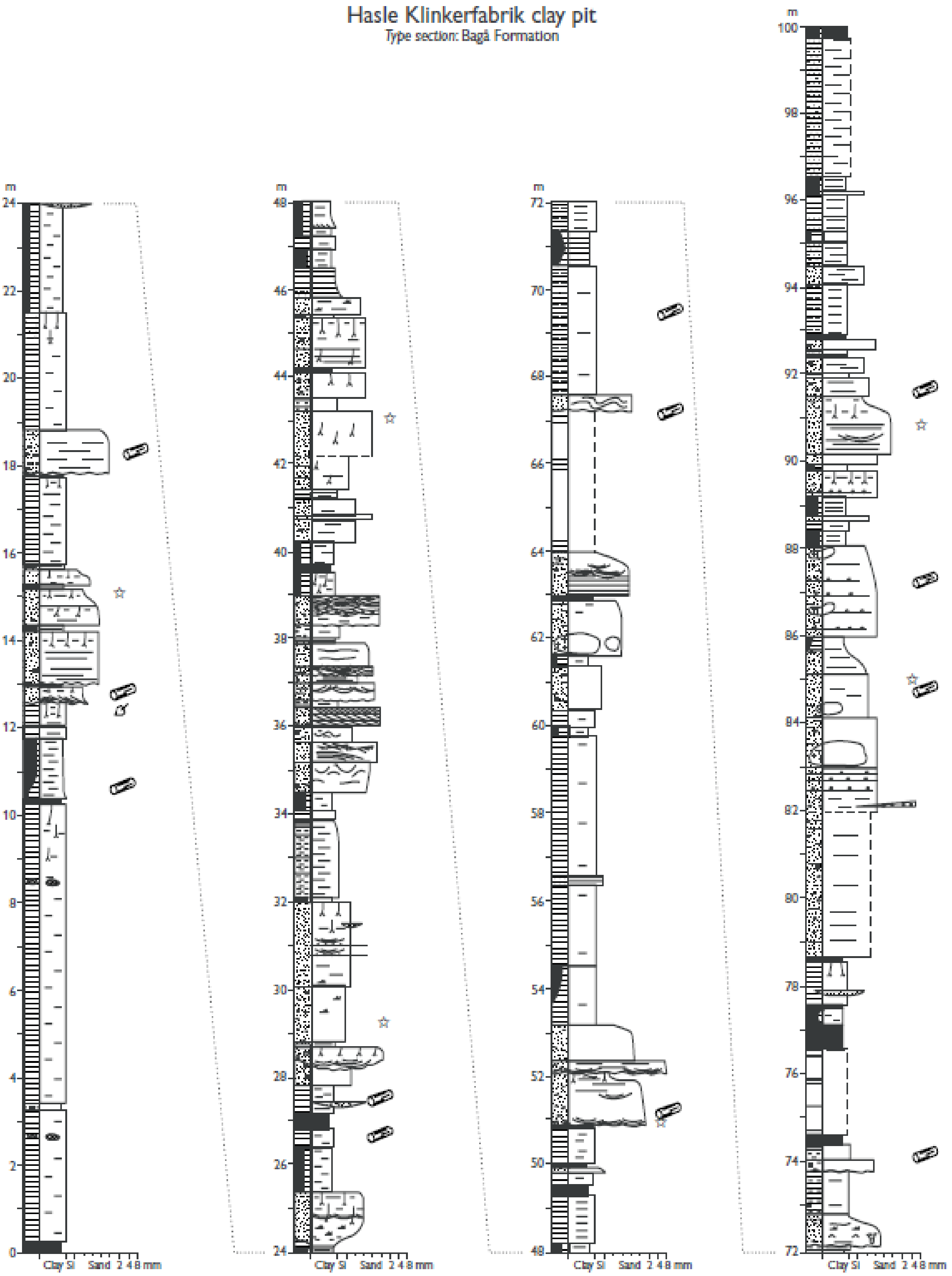


Figure 13 *Stratigraphic sections showing the lithologies in Hasle Klinkerfabrik clay pit After Koppelhus & Nielsen (1994).*

3 Kaolinite-rich clays in neighbouring countries

The alteration of rocks leading to formation of kaolinite alteration crusts and kaolinite-rich clays is not only seen on Bornholm but also and to a higher extent in our neighbouring countries.

3.1 Scania

Deep kaolinite weathering started in humid tropical climate of the Rhaetian period (Late Triassic *c.* 205 Ma) in Scania (Lidmar-Bergstrøm 1997). Weathering of bedrock continued in humid tropical to sub-tropical climate to until the Campanian Sea transgressed the area in the Late Cretaceous (c. 80 Ma). The altered rocks were covered by Late Cretaceous carbonates.

Quarrying the kaolinite started in late 19th century and formed the basis for e.g. production of e.g. sanitary ware from a pit on the northern tip of the island of Ivö, where the remains of china-clay (kaolinite) mines worked from the end of the nineteenth century until well into the 1950s can be found (Figure 14).

The resource is a clay- and silt-rich saprolite (a chemically weathered rock) with a kaolinite-dominated clay mineral association with chemically altered quartz grains.

Figure 14 *The kaolin clay pit at Ivö, Skåne. From Lidmar-Bergstrøm (1997).*

The kaolinite deposits in Scania have been explored by SG Ab in the 1980'ties by a large number of diamond exploration drillholes. The best area have been identified Markkula (1990) as the Billinge area where the deposit varies in thickness of 10 to 20 m and the overburden is *c.* 5 to 15 m. The total tonnage is estimated at c. 15 mill ton at a cut off at 20 % kaolinite. The detailed reports are stored at SGU (Geological Survey of Sweden), but has not been made available for this study.

3.2 Germany

The potentially interesting rocks in Germany can be divided into kaolinite alterations and kaolinite-rich clays that are formed by re-deposition of the kaolinite from the altered bedrock – as was the case on Bornholm.

3.2.1 Kaolinite in Germany

Primary kaolinite-rich rocks in Germany emerged through the weathering of feldspar or chlorite-rich rocks during periods with humid and a subtropical climate. The content of kaolinite decreases with increasing depth and lower weathering intensity.

The largest kaolinite deposits in Germany are located in Sachsen and Nord Bayern (Figure 15). The deposits in Northern Bayern were formed mainly by alteration of Triassic K-feldspar-rich sandstones (Elsner, 2017). An example is the very large one at Hirschau-Schnaittenbach is composed of *c.* 77 % quartz, 17 % kaolinite, 4 % K-feldspar and 2% muscovite, illite and various heavy minerals and the AKW company is mining c. 1.3 mill ton/p/a of ore here, producing c. 250.000 t/p/a refined kaolinite.

Figure 15 *Location of kaolinite deposits in Germany (Elsner, 2017).*

In Saxony feldspar bearing granites, gneisses, greywackes and sandstones were altered in three episodes of kaolinization *c.* 310 million years ago, 200 million years ago and 125-25 million years ago and now form up to 100 m thick kaolinitic weathering crust (Elsner, 2017).

The kaolinite deposits in Rhineland-Pfalz/Hessen/Nordrhein-Westfalen was formed 34-25 million years ago but to a large extent eroded and redeposited as kaolinite-rich clay deposits.

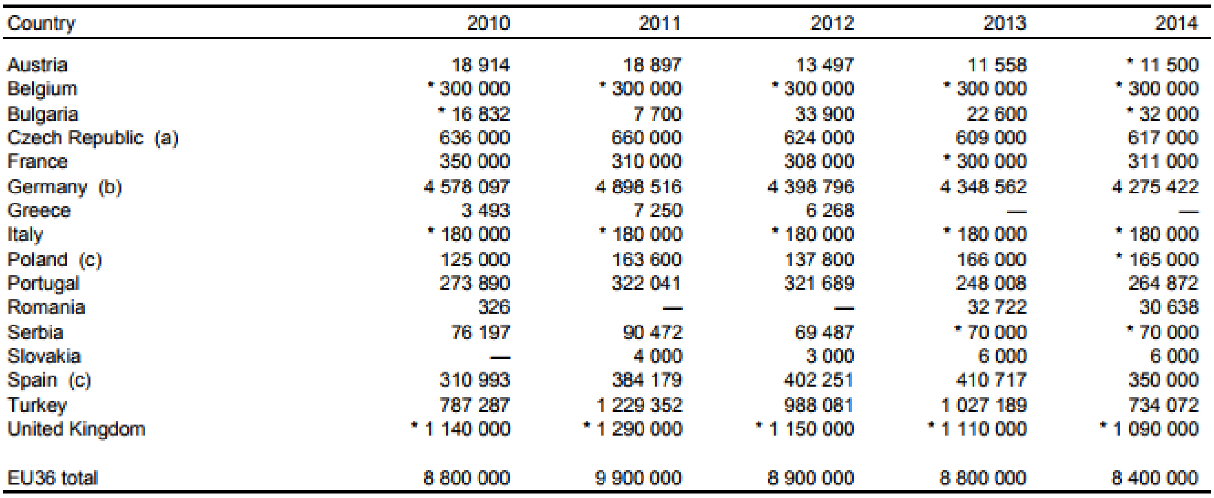
3.2.2 Kaolinitic clays in Germany

Kaolinitic clays formed when the kaolinitic deposits mentioned above were removed by erosion and transported to lakes, deltas or lagoons as the Jurassic deposits in Scandinavia. The formation of the clays in the Westerwald area occurred through intensive weathering of the older rocks in a subtropical climate 35 - 25 million years ago. The Westerwald clays have been mined since the 13th century and currently 13 companies operate 71 mines in the area (Figure 16).

In the Westerwald the starting point for the kaolinisation was mica-rich rocks and the clay deposits consists of a mixture of kaolinite, mica, illite and quartz.

Figure 16 *The Sibelco Petschmorgen clay pit. (Elsner, 2017).*

Table 1 *Production of kaolinite in Europe*



Country	2010	2011	2012	2013	2014
Austria	18 914	18 897	13 497	11 558	* 11 500
Belgium	* 300 000	* 300 000	* 300 000	* 300 000	* 300 000
Bulgaria	* 16 832	7 700	33 900	22 600	* 32 000
Czech Republic (a)	636 000	660 000	624 000	609 000	617 000
France	350 000	310 000	308 000	* 300 000	311 000
Germany (b)	4 578 097	4 898 516	4 398 796	4 348 562	4 275 422
Greece	3 493	7 250	6 268	—	—
Italy	* 180 000	* 180 000	* 180 000	* 180 000	* 180 000
Poland (c)	125 000	163 600	137 800	166 000	* 165 000
Portugal	273 890	322 041	321 689	248 008	264 872
Romania	326	—	—	32 722	30 638
Serbia	76 197	90 472	69 487	* 70 000	* 70 000
Slovakia	—	4 000	3 000	6 000	6 000
Spain (c)	310 993	384 179	402 251	410 717	350 000
Turkey	787 287	1 229 352	988 081	1 027 189	734 072
United Kingdom	* 1 140 000	* 1 290 000	* 1 150 000	* 1 110 000	* 1 090 000
EU36 total	8 800 000	9 900 000	8 900 000	8 800 000	8 400 000

Source: European Minerals Statistics. BGS

4 Bauxite

Bauxite is formed by extremely intense alteration of the existing rocks in hot and humid climate and there are two types: Lateritic bauxites (silicate bauxites) and karst bauxite ores (carbonate bauxites).

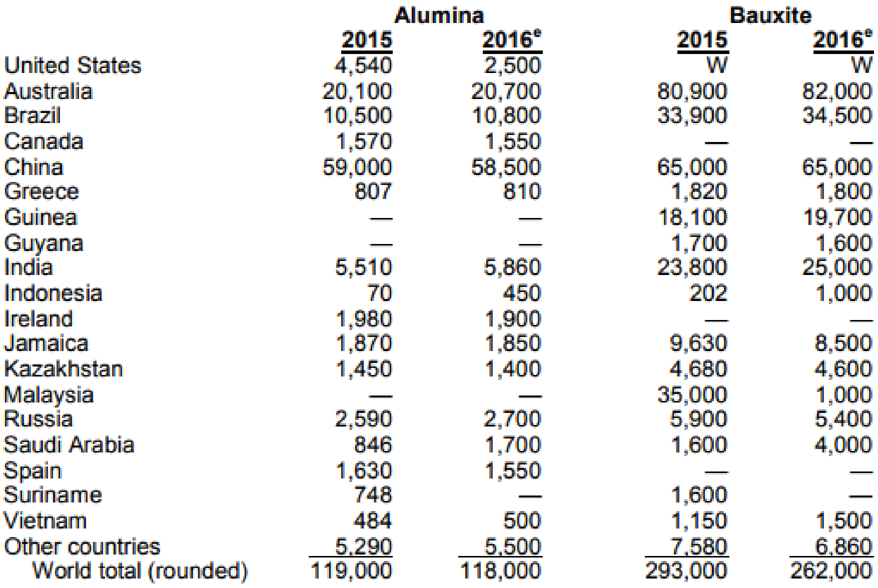
The carbonate bauxites occur predominantly in Europe, Guyana, and Jamaica above carbonate rocks (limestone and dolomite), where they were formed by dissolution of the carbonates and accumulation of intercalated clay layers.

The lateritic bauxites are found in the tropics. They were formed by alteration (lateritization) of silicate rocks such as granite, gneiss, basalt and shale in areas with very good drainage. The aluminium minerals in the bauxite are mainly gibbsite ($Al(OH)_3$), boehmite ($AlO(OH)$) or diaspore ($AlO(OH)$). The differences in the bauxite composition stems from the composition of the precursor – i.e. the rock that was altered.

Specific surface (BET) area of Bauxite is between 10 and 20 m^2/g (Li & Rutherford 1996).

Bauxite is mined in very large quantities at locations with good access to harbour facilities that take large boats, and the price for bauxite delivered is low. An example is F.A.S. USA is *c.* 30 US$ = 182 DKK (USGS Mineral Commodity Summaries 2018). Import to e.g. Studstrupsværket which can take big ships could be ca. at this price.

Table 2 *World production of alumina and bauxite (1000 t)*



	Alumina		Bauxite	
	2015	**2016e**	**2015**	**2016e**
United States	4,540	2,500	W	W
Australia	20,100	20,700	80,900	82,000
Brazil	10,500	10,800	33,900	34,500
Canada	1,570	1,550	—	—
China	59,000	58,500	65,000	65,000
Greece	807	810	1,820	1,800
Guinea	—	—	18,100	19,700
Guyana	—	—	1,700	1,600
India	5,510	5,860	23,800	25,000
Indonesia	70	450	202	1,000
Ireland	1,980	1,900	—	—
Jamaica	1,870	1,850	9,630	8,500
Kazakhstan	1,450	1,400	4,680	4,600
Malaysia	—	—	35,000	1,000
Russia	2,590	2,700	5,900	5,400
Saudi Arabia	846	1,700	1,600	4,000
Spain	1,630	1,550	—	—
Suriname	748	—	1,600	—
Vietnam	484	500	1,150	1,500
Other countries	5,290	5,500	7,580	6,860
World total (rounded)	119,000	118,000	293,000	262,000

Source: Source: USGS Mineral Commodity Summaries 2017

5 Waste products from other industrial processes

5.1 Red mud

To make aluminium bauxite ore is heated in a pressure vessel along with a sodium hydroxide solution at a temperature of 150 to 200 °C. The aluminum is then dissolved as sodium aluminate, with sodium hydroxide at elevated temperature and pressure (the Bayer process). The insoluble product after the bauxite digestion is called Red Mud, which is a mixture of compounds originally present in the parent bauxite together with compounds formed during the Bayer process. The Red Mud is disposed as a slurry having a solid concentration in the range of 10-30%, pH in the range of 13 and high ionic strength. There is a wide variation in chemical composition in Red Muds worldwide depending on the composition of the bauxite that was used as well as how well e.g. NaOH is recovered. Typical values of Red Mud from India and Brazil is given as in Table 3 (no compositions of European Red Mud was available):

Table 3 *Chemical composition of red mud generated at different plants in India and Brazil*

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	Na_2O	LOI
HINDALCO Renukoot	7,5	21,9	15,6	28,1	10,2	4,5	12,2
BALCO	7,3	19,4	16,4	27,9	11,8	3,3	12,6
NALCO Damanjodi	6,4	14,8	3,7	54,8	2,5	4,8	9,5
INDAL Belgam	7	19,2	13,5	44,5	0,8	4	10
Brazil BM1	1,4	6,8	7,8	71,6	3,2	0,4	8,7
Brazil BM2	0,6	7,9	10,9	65,3	5	0	10,4
Brazil BM3	0,8	10,8	8	64,6	2,9	0,1	12,8
Brazil BM4	2,3	12	9,1	62,2	3,2	0,7	10,5
Brazil BM5	3,4	9,4	10,4	61,7	4,2	1,5	9,5
Brazil BM6	0,8	13,5	9,3	60,4	3,2	0,4	12,5
Brazil BM7	3,8	7,8	3,6	65,7	3,6	1,4	8,1

Indian data from Samal et al. (2013) Brazilian data from Li & Rutherford (1996).

The minerals that compose Red Mud are hematite, goethite, gibbsite, boehmite, diaspore, calcite, calcium aluminum hydrate, quartz, rutile, anatase, kaolinite, sodalites, cancrinite, hydroxycancrinite, chantalite, hydrogarnet. The content of Na in the Red Mud is from the Bayer process and the aluminium smelter will try to recover as much as possible. As seen in Table 3 with better success in Brazil compared to India. Red Mud is a very fine-grained material with 90 % below 75 µm, and the specific surface (BET) of Red Mud is around 20 to 50 m^2/g (Chvedov et al. 2001; Li & Rutherford 1996).

The production of Red Mud is c. 150 millions of ton per year world wide (Evans 2016). As Red Mud is a by-product of which there is little use today, it is likely that it can be acquired for the cost of moving it. It has not been possible to find information on previous use of Red Mud as an additive in wood combustion. The positive features apart from the low price are the fine grain-size, large specific surface, and high content of aluminium. It is not known to what extent e.g. potassium will react with the iron in a boiler, but if it form e.g. potassium ferrate, this is described as having properties such as high stability, oxidizing power, selectivity, and a non-toxic by-product Fe(III), that make potassium ferrate(VI) an environmentally friendly oxidant for natural waters (Sharma, 2002).

5.2 Mining and quarrying

5.2.1 Denmark

In most quarries and gravel pits in Denmark and surrounding countries the main target is aggregate for e.g. concrete production, and the fine-grained fraction i.e. < 2 mm is a waste product. At the Dansand quarry in Addit south of Silkeborg, the main product is silica sand, and there is only a small market for the fine fraction < 0,2 mm available as a semi-dry product. This product has a high content of kaolinite and is likely to be well suited as an additive. However, the total production is limited to *c.* 3.000 t.p.a.

In most gravel pits in Denmark, the fine fraction < 2 mm will mainly consist of fine sand and slit with a minor clay component. The sand and silt will be composed mainly of quartz, feldspar and heavy minerals, and the < 2 mm fraction will contain Na and K in the feldspars.

The content of reactive minerals is accordingly likely to be low as well as the specific surface area (BET), but amount of data available is very limited. The advantage of the < 2 mm fraction is that this material is easily available because there is very limited market for it and there will be gravel pits close to the power plants.

5.2.2 Neighbouring countries

Along the coast of Norway there are a number of quarries that produce aggregate (crushed rock) for export. These quarries often have excess of the fine-fraction < 2mm. The composition of this material varies with the quarried rock-type. Granitic compositions will be close to what is found in the Danish gravel pits. When the composition is more “mafic” i.e. with less SiO_2 as e.g. the “hyperite” in the Valberg quarry located at the Valberg peninsula in the community of Kragerø, on the south-eastern coast of Norway. This rock is classified as a gabbro norite, contains no quartz, very little feldspar, low contents of alkali metals and have a high melting point. Accordingly, the 0 - 2mm fraction from this quarry could be a candidate.

5.2.3 Kaolinitic overburden and tailings

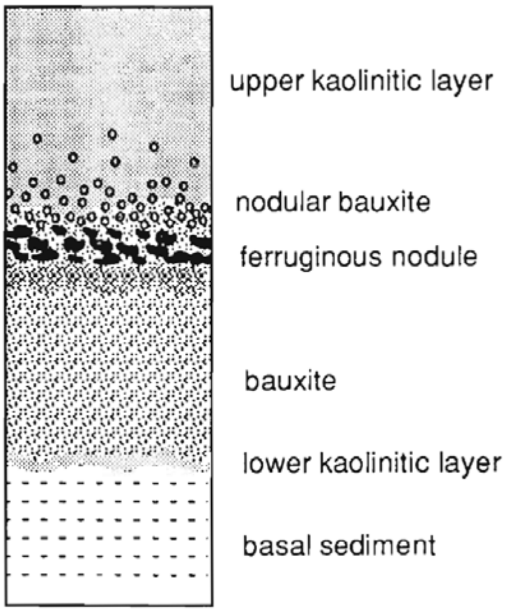
Kaolinite rich alteration surfaces are very common in tropical climates. Locally they occur on top of or together with rocks that are mined - and will have to be removed during the operation. At such places there will be a logistic solution to how the kaolinite can get on a boat to Denmark and available for use e.g. as an additive in wood combustion:

Porto Trombeta

At the Porto Trombeta bauxite mine there is a c. 10 m thick overburden over the bauxite very rich in kaolinite. This layer have to be removed to get to the bauxite, and there may be a chance to buy this material at a low price.

The bauxite is mined on a large plateau, and the geology is rather uniform on the whole plateau with the same sequence of horizons all over the plateau (Boulangé & Carvalho 1997). The thickness of the “upper kaolinitic layer” (Figure 17) varies from 8 to 10 m and it is constituted mainly of kaolinite (80 %), gibbsite (10 %) and quartz (10 %) (Boulangé & Carvalho 1997).

If this is available, it could be a possible additive.



Figur 17

Typical profile in the Porto Trombetas deposit (Boulangé & Carvalho 1997)

Table 4 *Composition of upper kaolinitic layer*

	1	2	3	4
SiO_2	38,9	37,1	36,5	34,5
Al_2O_3	34,8	36,3	36,9	37,9
Fe_2O_3	8,4	8,6	8,2	7,9
TiO_2	2,7	2,8	2,8	2,8
H_2O	15	14,8	15,2	16,5

6 Cost of the additive

The main cost factors to consider are price at the source, the costs of bringing the additive to the power plant, the content, and the effectiveness of active minerals in the material.

6.1 The price of the product

The price of the additive/cost of production of it on the mine-site is mainly dependent on the amount of overburden over the deposit (cost of removal) and environmental cost (assuming that there is no processing of the additive at the mine-site). The cost in the quarry will roughly be in the order of magnitude of 50 to 100 DKK/ton of unprocessed clay.

However, it is nessesary to take the content of active additive minerals in the raw product into account. A brief compilation of some of the possible additives is listed in Table 5.

Table 5 *Composition of selected raw materials*

	Sibelco	Sibelco	Schmidt	Goerg Sch.	Gram Fm.	Lillebælt	Holmehus
Locality	Westerw.	Kaolin	Westerw.	Westerw.	Gram	Hinge	Avg. DK.
> 63 µ	2	13	5	25	5	0	2
63 µ - 2 µ	31	47	45	45	73	14	20
< 2 µ	67	40	50	30	23	86	78
Kaolinite	37	43	35	18	18	21	1
Illite etc	24	8	20	48	15	33	10
Smectite					18	26	65
Quartz	34	44	45	27	43	10	10
Other	2	2		7	6	10	12

The product will have a content of water – if not dried at the site.

6.2 The transport to the power plant

Transport of a semi-dry product will include the cost of transporting the content of water. However, the transport can be as a bulk product, whereas dry products often have to be transported e.g. in powder tankers etc. which is much more expensive.

The distance from pit to power plant. Here there is further an important issue – namely if it is possible or viable to transport on ship. There are some very rough numbers:

- Transport in truck cost c. 1 DDK per km per ton.
- Transport on boat from e.g. a harbor at the Rhine (Westerwald) will cost *c.* 130 DKK/ton (20 US$) whereas transport on a boat from Brazil to Studstrup could cost *c.* 250 DKK/ton (depending on the market situation).

A very rough calculation of different scenarios just to get an idea of the orders of magnitude of the cost involved:

Table 6 Rough estimates of costs of bringing additive to power plant

Source	**Plant**	**Quarry** DKK	**Truck** DKK	**Boat** DKK	**Handling** DKK	**Raw ton** DKK	**Act. min.** %	**Act. min.** DKK/ton
Hinge	Studstrup	75	30		10	115	80	194
Hinge	Avedøre	75	30	100	30	235	80	397
Gram	Studstrup	75	157		10	242	51	641
Gram	Avedøre	75	40	100	30	245	51	649
Kaolin Scania	Studstrup	100	30	110	30	270	60	608
Kaolin Scania	Avedøre	100	164		10	274	60	617
Westerwald	Studstrup	100	40	130	30	300	61	664
Westerwald	Avedøre	100	40	130	30	300	61	664
Raw Bauxite Brazil	Studstrup	100		250	30	380	80	641
Raw Kaolin Brazil	Studstrup	100		250	30	380	80	641

The main point in the above very rough estimates of the price of bringing additives to the power plants is that the cost of the different additives does not vary a lot when the content of active minerals is considered. The column to the right in Table 6 is calculated assuming an estimated content of active minerals (Act. Min. (clays in Table 5)) and a content of 30 % water in the raw additive.

The clay from Hinge is cheap compared to the other alternatives because it has a very high content of clay and because of the proximity to Studstrup.

6.3 Storage and processing at the power plant

In the Danish climate, it may be a consideration if the clay/additive should be stored under roof. If the additive is carried by truck to the power plant, storage at the power plant is not a big issue, but if it is received, e.g. on *c.* 15.000 t ships the cost of storage facilities should be taken into account.

It is assumed that the additive can be mixed mechanically with the wood pellets, ground in the mill together with the wood pellets and during this operation be brought to a form where it can be introduced into the boiler. Fine-grained materials will probably not profit from this grinding, whereas e.g. the 0 – 2 mm fraction from quarries would benefit from this grinding.

Some clays are sticky when wet, and this may have to be taken into account in handling the additive. If there is excess heat at the power plant, it may be relevant to dry the additive before mixing it with the wood pellets for easier handling.

The natural clays are a mixture of different clay minerals at their origin, a mixture that varies among the different deposits and even within the individual deposits. It can be considered, if it could be viable to mix clays from different sources to get the optimal and most cost effective mixture of minerals and grain-sizes in the additive that is introduced into the boiler together with the wood pellets.

7 Summary

Alkali metals released to the gas phase from wood during combustion in PF boilers cause slagging, fouling and corrosion problems in the boiler and de-activates de-NOx SCR catalysts. This can be abated by injection of additives into the wood boilers such as kaolinite or coal fly ash. However, refined kaolinite is expensive, and because coal will be phased out from Ørsted boilers new types of additives is wanted. The objectives of this report have been to make a rough screening of possible low cost raw materials as alternative additives in this process.

There is a range of possible additives in Denmark and neighboring countries some. The most clay-rich types (Holmehus Formation and the Lillebælt clay, Table 5) have a high content of smectite. They are likely to be very reactive, but the behavior under conditions in the boiler is not known. The clay-type with the highest proportion of kaolinite relative to the other clay-minerals is the Gram Formation found in southern and western Jutland. This clay have been used to make bricks that can be fired to 1250°C without melting, and it is considered likely that this raw material could be used as an additive.

Kaolinite-rich clays in southern Sweden together with Jurassic clays on Bornholm have been used for making bricks that can withstand high temperatures and are obvious targets for further prospecting for additives near the Danish power plants. Kaolinite-rich clay from Germany are also known to withstand high temperatures in tiles manufacturing and because it has high absolute contents of kaolinite and other clays that probably will combine with the alkalis during the combustion.

Kaolinite-rich raw materials and bauxite occur in hot and humid climates and can be acquired and transported to Denmark at relatively low costs. The proportion of active minerals are high in these materials and it must be considered, if the cost of transporting these raw materials to Denmark is balanced by a higher content of active minerals.

Residual from production of aluminium, the so-called Red Mud contain aluminium, have a very high surface area and will be inexpensive. Accordingly, this will form a possible alternative to primary raw materials as additive. Other residuals such as rock flour i.e. fine-grained by product from aggregate production in Norway could also be a relevant alternative to primary raw materials.

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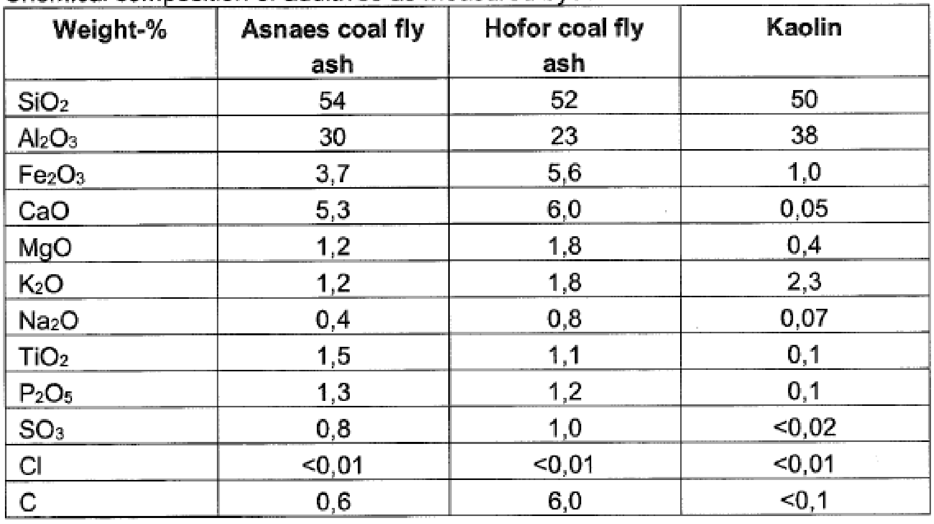
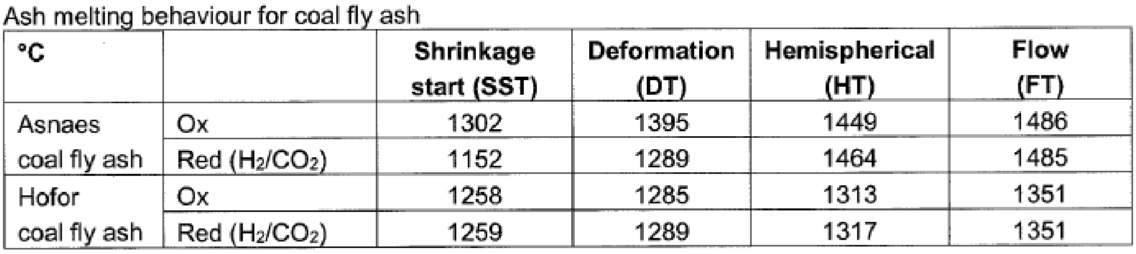
Appendix 1

Chemical composition of additives as measured by XRF



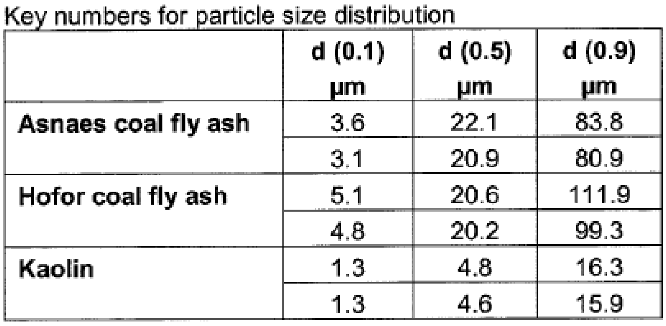
Weight-%	Asnaes coal fly ash	Hofor coal fly ash	Kaolin
SiO_2	54	52	50
Al_2O_3	30	23	38
Fe_2O_3	3,7	5,6	1,0
CaO	5,3	6,0	0,05
MgO	1,2	1,8	0,4
K_2O	1,2	1,8	2,3
Na_2O	0,4	0,8	0,07
TiO_2	1,5	1,1	0,1
P_2O_5	1,3	1,2	0,1
SO_3	0,8	1,0	<0,02
Cl	<0,01	<0,01	<0,01
C	0,6	6,0	<0,1

Ash melting behaviour for coal fly ash



°C		Shrinkage start (SST)	Deformation (DT)	Hemispherical (HT)	Flow (FT)
Asnaes coal fly ash	Ox	1302	1395	1449	1486
	Red (H_2/CO_2)	1152	1289	1464	1485
Hofor coal fly ash	Ox	1258	1285	1313	1351
	Red (H_2/CO_2)	1259	1289	1317	1351

Key numbers for particle size distribution



	d (0.1) µm	d (0.5) µm	d (0.9) µm
Asnaes coal fly ash	3.6	22.1	83.8
	3.1	20.9	80.9
Hofor coal fly ash	5.1	20.6	111.9
	4.8	20.2	99.3
Kaolin	1.3	4.8	16.3
	1.3	4.6	15.9