Gypsum $CaSO_4 \cdot 2H_2O$

1. The importance of gypsum

Gypsum is one of the oldest known minerals used in basic and construction materials. As far back as 7000 BC, gypsum was already used as a base for frescoes in the town of Catal Huyuk in Asia Minor.[16] Gypsum was also used in its natural form for sculptures and building blocks, as plaster and in the mortar of world-famous buildings such as the towers of Jericho, the Great Pyramid of Cheops or the Palace of Knossos.[8]

The Romans knew about the advantageous properties of gypsum and spread the knowledge about its preparation to the area north of the Alps.[7] Much of this knowledge about the processing of gypsum was lost during the Migration Period (400–700 AD) . It was not until the architectural style of Romanticism that gypsum returned to the scene as a building material. Gypsum technology was further developed during the period of industrialisation in the 19th century, which provided a clear distinction between gypsum dihydrate, hemihydrate and completely dehydrated anhydrite and the importance of different firing temperatures (Chap 5, Tab. 1).[7]

The world production of gypsum is in range of 140–160 million tonnes (Fig. 2).[5,23] Gypsum and anhydrite occur all over the world and are usually easy to exploit.

In global terms, around 50 % of the gypsum is used for the production of cement, 39 % for the production of plaster and stucco (which also includes wallboards) and around 10 % in agriculture (Fig. 1).[22] Due to its low price (Fig. 2) gypsum and gypsum products are not usually transported over long distances, which in the past prevented the recycling of gypsum waste. During the past few years better technologies were developed for the increased recycling of gypsum.[11]

In regions where there are coal-fired power plants, these recycled products have to compete with cheap flue-gas desulfurization (FGD) gypsum (Chap. 3).

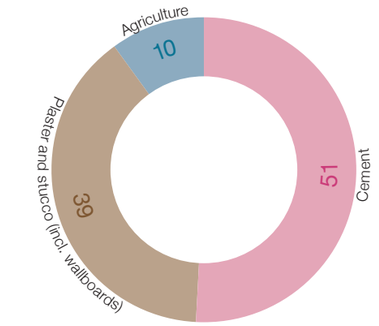


Fig. 1 Global use of gypsum in 2004 as a percentage (22).

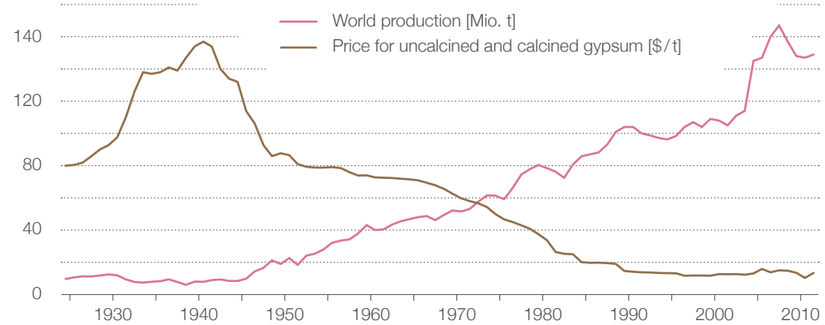


Fig. 2 Global gypsum production and price trends of calcined and uncalcined gypsum (23) U.S. market price, adjusted for inflation, reference year 1998.

2. Understanding the system

Despite having rich gypsum deposits in Switzerland, just over 50 % of the gypsum required in the form of finished products such as plaster-/wallboard (for drywalling) and building plaster as well as raw gypsum for the production of cement is imported (Fig.3). Switzerland requires around 840 000 tonnes of gypsum a year, which corresponds to almost 100 kg/(per capita/ year).[19] In neighbouring Germany, this figure is around 120 kg/(per capita/ year).[1,5] At approximately 20 kg/(per capita/ year)[3], the global average is significantly lower. Almost all gypsum is used in construction (gypsum used for modelling and as fertilizer is negligible is terms of quantity). About 240 000 tonnes of gypsum leave the building stock in Switzerland every year.[17] This represents about 30 % of the entire demand for gypsum. Thus the gypsum building stock increases annually by a round 600 000 t (~ 73 kg/per capita).

Today, around 27 million tonnes of gypsum are in use in constructions in Switzerland, which corresponds to slightly more than 3 t of gypsum per capita. Between 2000 and 2012, the use of gypsum has increased by almost 50 %.[19] This trend is likely to continue due to increased gypsum use in drywall construction. The demand for gypsum wall materials today in Switzerland is in the range of 1.7 m^2/(per capita/ year), while in Germany it is around 2.8 m^2/(per capita/ year) and in France 3.5 m^2/(per capita/ year).[4] On this premise, the stock of gypsum in Switzerland could grow to over 45 million tonnes by 2035.[19] The recovery of gypsum in Switzerland today is still at a modest level: approx. 4 000 t/yr.

Over 250 000t of gypsum waste ends up in landfills every year. Due to the strong growth of this waste stock and the lack of countermeasures, this material stream will increase sharply in the future. Due to the environmental problems of landfilling gypsum, efforts are being made across Europe to strengthen the incentives to recycle gypsum.[6,10]

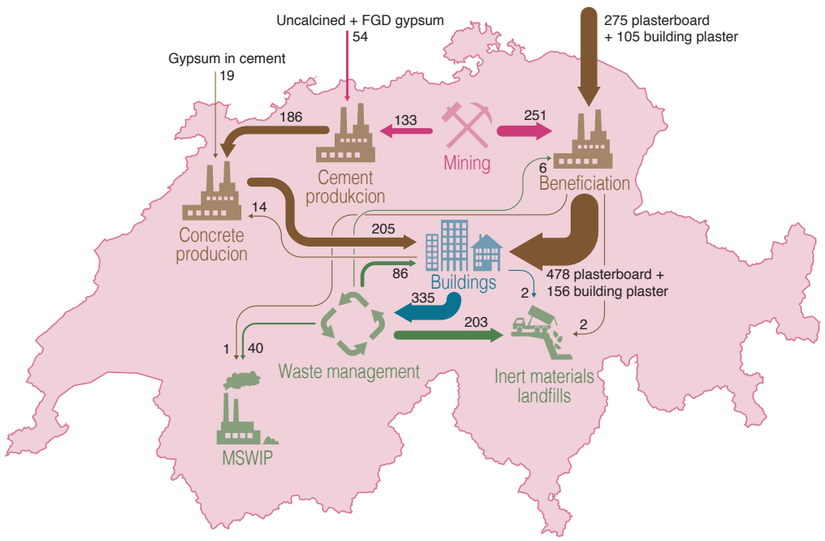


Fig. 3 Gypsum streams in Switzerland in 2013 (19). In 1000 tonnes.

7. Society

Gypsum is one of the mineral resources in Switzerland which have a good long-term availability. Nevertheless around 50 % of gypsum products are imported and thus most of the value creation is generated abroad. The reason for is, that products such as plasterboard are produced in bulk. In mass production, low labour costs are particularly crucial in order to be competitive in the world market. This condition is not fulfilled in Switzerland.

On the other hand, due to a high growth in stock there is more and more gypsum waste. This wastage ends up in the inert material landfills, where the sulphate can be washed out and can enter the groundwater or the landfill waste water. In addition, the aivailable landfill volume should be conserved where possible. Given its physical and chemical properties, gypsum can in principle be managed as a sustainable resource.

Especially nowadays, that sustainable building has become the current trend, the gypsum industry should make better use of the recycling potential. Plasterboard can be recycled to a high degree, which could be a major societal selling point over other wall materials that have a much lower potential for being recycled.

Due to the high percentage of imports, it will become more and more difficult to reuse all of the future gypsum waste in Switzerland.

In addition to the production of gypsum wallboard, the cement plants are, first and foremost, the target processes for the recycling of gypsum. In theory this would represent a consumer market of around 200 000 t/yr. In the longer term, however, the Swiss gypsum waste collection and processing capacities capacities have to be increased and additional waste material purchasing markets have to be developed abroad. This could mean that society must formulate the conditions such that, for example, the companies producing abroad will have to take back a certain percentage of waste gypsum and use it in their production on a long-term basis. Alternatively Switzerland could consider an increase of own recycling and production capacities, coupled with a reduction of imports.

Other measures and courses of action that lead to a prevention of environmental impacts and a more sustainable use of gypsum must be discussed and driven forwards in cooperation with the gypsum and cement industries, as well as with the importers of gypsum products. As a forward-looking stakeholder, the public sector should moderate and assist the process development towards attaining a sustainable resource management in the gypsum industry.

8. Resource management: The overall situation at a glance

The recycling rate of gypsum waste from construction materials is still only in the range of a few percent. Gypsum in concrete and in plasters as well as screeds can barely be recycled, or only at great expense. This is not the case for wallboard and plasterboard, where the impurity levels are low and therefore so are the processing costs.

There is potential to massively increase the recycling rate. The cement industry in particular offers huge opportunities in terms of quality requirements and sales potential (approximately 200 000 t/yr). The the public sector can initiate and support the first phase of this process. In parallel with this, the (legal) boundary conditions which promote the recycling of gypsum waste could be improved, if necessary. If this succeeds, the gypsum and cement industries can use the perception of RC-gypsum as a more sustainable building or raw material for marketing in their own gain.

Further need for action by the public sector stems from the opportunity to preserve free landfill space to a considerable extent if gypsum were reused. Furthermore, this will also avoid long-term emissions of SO_2 into the air.

However, the low price of primary and FGD gypsum impede recycling.

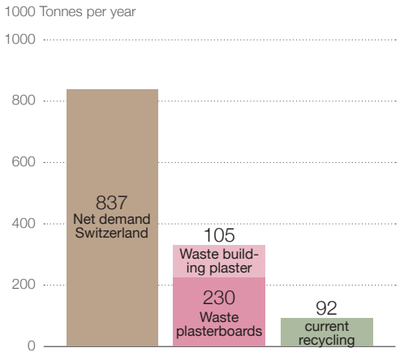
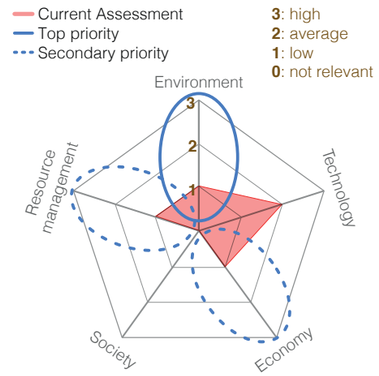


Fig. 8 Comparison of the annual gypsum requirement and recycling potential with the current recycling.

Open issues

1. Validation of the model for describing the gypsum flows in Switzerland
2. State of the gypsum recycling technology with respect to source and target processes
3. Potential for the export of RC gypsum
4. Evaluation of the collection systems and sites for the processing of RC gypsum



▶ Fig. 9 Evaluation of the recycling potential of gypsum based on a qualitative expert assessment.
Criteria: *Environment*: 'Final sink landfill', discharge conditions problematic with landfills for inert materials; *Technology*: no technology for the recovery of building plaster, yes for plasterboard; *Economy*: Recycled gypsum is significantly more expensive than primary or FGD gypsum; *Society*: not relevant; *Resource management*: recycling is currently only economic to some extent, but it could make sense to introduce a recovery obligation.

Literature
Due to limited space, the bibliographic references are summarised in a separate document.

http://daten.sgtk.ch/rohstoff-monitoring/AWEL_Gypsum_Literature_EN.pdf

This substance dossier was created by Stefan Rubli (Chapter 4 supplemented by Elmar Kuhn) in collaboration with the Swiss Geotechnical Commission SGTK and the GEO Partner AG for the AWEL.

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3. Primary/secondary raw materials

Switzerland has large geogenic deposits of gypsum that are found mainly in the Triassic deposits of the Jura region and the Alps. [17] The gypsum rock is currently being mined in Bex (VD), Granges (VS), Leissigen (BE) and Kerns/Melbach (OW) in open- pit mines.[21] After excavation the gypsum rock is treated (Leissigen or Granges) and ends up either in the cement factories or is processed into hemihydrate and anhydrite using the single-, double- or high-firing method. The product is then manufactured into wallboard (at Leissigen and Granges) or gypsum plasters and mortars (at Kerns, Melbach, Bex and Granges).

As byproducts of industrial processes large quantities of gypsum are mainly produced abroad by means of flue-gas desulphurisation (FGD gypsum) in coal-fired power plants. In Germany alone, the produced quantities of industrial plasters have risen sharply following a regulation for large combustion plants, and are currently in the range of 7–8 million t/yr.[9] At European level, around 15 million tonnes of gypsum were produced in 2003.[12]

FGD gypsum is powdery and has a residual moisture content of 10 %.[17,1] Natural gypsum and FGD gypsum have the same chemical composition (except Hg and Se). Because it is not grainy like natural gypsum, FGD gypsum has to be dried and briquetted. This process requires 150 kWh / t for the drying and 10 kWh / t for the briquetting.[12] Hardly any FGD gypsum is produced in Switzerland, however, some is imported from neighbouring countries to produce cement (Fig. 3).

Dismantling and renovation activities of the building- and deconstruction industry produce large amounts of gypsum waste. Today, some 280 000 tonnes of are likely to accrue every year in Switzerland, an amount which could almost double by 2035 (Fig. 4).[19]

From the recycling point of view, the gypsum plasterboard (wallboard) used in drywalling are particularly of interest. They result in over half of the total gypsum waste (Fig. 4). In Switzerland a recycling system for waste gypsum has been operating for several years.[18] The waste is first collected in various recycling centres and then sorted. From here it goes into the processing plant at the wallboard production site. The recycled gypsum is fed in the production process together with the primary material. Currently, the recycled content of the produced gypsum wallboards is in the range of only 2 %, a percentage that could be significantly increased. However, the total volume of wallboards produced in Switzerland is too small to accommodate all of the potentially recoverable waste gypsum, which currently amounts to around 230 000 t (Fig. 3). The cement industry in turn could be a promising buyer of recycled gypsum because it requires rather a lot of gypsum, approximately 200 000 t /yr. Additionally, the cement manufacturing process specifically needs calcium sulphate dihydrate (Chap. 5, Tab. 1). The mechanically prepared gypsum could therefore be used without further processing.

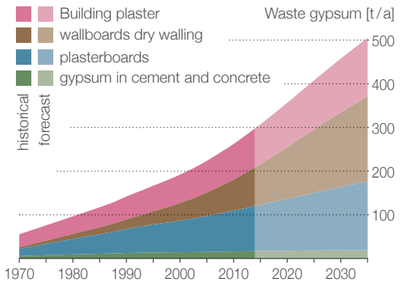


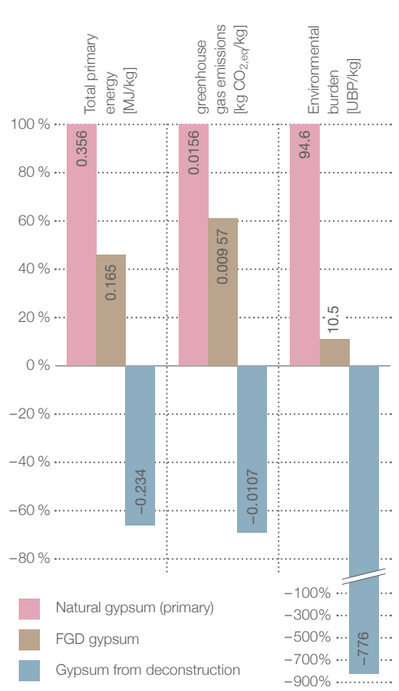
Fig. 4 Development of gypsum outputs from construction in Switzerland (stacked)(19).

4. Environment

Depositing gypsum in landfills is problematic due to its environmental impact potential. Gypsum reacts with water and the dissolved sulphate (SO_4^{2-}) seeps down as landfill leachate, thereby making the direct discharge of the collected wastewater into a smaller outfall canal very problematic.[2]
The AWEL has defined the quality objective for surface waters containing sulphate at maximum 100 mg / l. Throughout Switzerland, almost half of the landfills for inert materials produce leachate with sulfate contents over 600 mg / l.[3]

Surface waters containing sulphate in concentrations exceeding 600 mg / l are considered to be very aggressive to concrete and thus detrimental to the sewage systems and hydraulic structures. Under reducing conditions, the sulphate can be reduced to sulphide (S^{2-}), forming hydrogen sulphide (H_2S) in aqueous solutions. Hydrogen sulphide is a volatile compound and degasses.[15] It is very toxic and can be microbially converted to sulphuric acid in the aerobic condensation water of the canal wall. This process causes corrosion damage in concrete canals, pumping stations and installations.[3]

A life cycle assessment shows that gypsum accrued as by-product of industrial processes ist significantly more environment friendly compared to the production of primary gypsum.[24] Flue-gas desulphurisation (FGD) gypsum for instance only accounts for 11% of the environmental impact, compared to that of the primary production of gypsum. It is in every respect (energy consumption, emissions, environmental impact) striking to see how worthwhile it is to recycle gypsum from construction debris: −820 % (!) of the environmental impact points caused by gypsum primary production could be avoided. However, this is not because of a dubious primary production process; the significant environmental advantage of recycling gypsum from construction waste is that it does not have to be disposed of into landfill sites (see above).[24]



▶ Fig. 5 The life cycle assessment of primary (pink) and secondary gypsum from the flue-gas desulphurisation residues (brown) and from building demolition (blue) (24) Normalised to primary gypsum (= 100 %). Negative numbers arise from the huge benefits of avoiding the landfilling of building demolition material containing gypsum compared to the comparatively small impacts of recycling.

5. Technology

The preparation of the various gypsum products can be defined as a gradual expulsion of the water bound in the gypsum rock ($CaSO_4 \cdot 2\,H_2O$).[17] Depending on what products are to be made, the gypsum is partially or completely dehydrated as follows:

1) $CaSO_4 \cdot 2\,H_2O \longrightarrow CaSO_4 \cdot ½H_2O + 1½H_2O$ (T ≤ 130 °C)
2) $CaSO_4 \cdot ½H_2O \longrightarrow CaSO_4 + ½H_2O$ (T ≥ 160 °C)

During the manufacturing, this process can be reversed by adding water. Four phases of the system $CaSO_4$ / H_2O are relevant for the production of gypsum (Tab. 1). These differ primarily in the amount of crystal water, the stability and the formation temperature.

The phases are contained in the various gypsum products in different compositions (Fig. 6). When gypsum has not been thermally treated, it is used as a set regulator in the cement industry and as a sulphate carrier in the chemical industry. β-hemihydrate is used to produce gypsum plasterboard, gypsum wallboard and indoor plaster; plaster of paris also contains anhydrite II. Screeds (underlay for floors) are divided into anhydrite and gypsum screeds. They contain, among other additives, anhydrite, α-hemihydrate or a mixture. Plaster for moulding and modelling is made from α- and β-hemihydrate.[1]

Tab. 1 Phases of the system $CaSO_4/H_2O$.

	Gypsum	"Hemihydrate"	Anhydrite III	Anhydrite II
Chemical name	Calcium sulphate dihydrate	Calcium sulphate hemihydrate	Calcium sulphate	Calcium sulphate
Chemical formula	$CaSO_4 \cdot 2\,H_2O$	$CaSO_4 \cdot ½\,H_2O$	$CaSO_4$	$CaSO_4$
Forms		α and β	α and β	
Water content [M%]	20.92	6.21	0	0
Formation temperature:		α: 80–180 °C, β: 120–180 °C	α: 100 °C, β: 290 °C	300-900 °C

Due to its chemical properties, gypsum is principally easy to recycle, because the hydrated gypsum fractions can be dehydrated by heating. However, the gypsum waste should not contain high levels of impurities (cf. supplement). Therefore, one could start with the recycling of wallplaster and plasterboard[13].

The energy required for this process is relatively low because the material only has to be broken up and ground as in the primary production. The cardboard can be separated from the plasterboard by means of sieving.

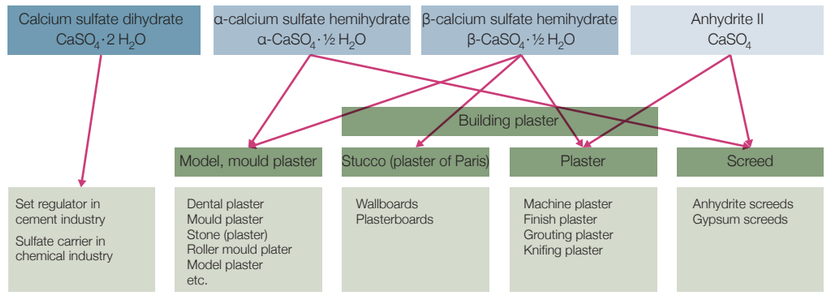


Fig. 6 Flow sheet for gypsum products (1).

6. Economy

In 2013, approximately 435 000 t of gypsum products were imported, but only small amounts were exported (Fig. 3).

The largest share of the imports was made up by wallboard with approximately 275 000 t, followed by building plaster at 105 000 t, whilst the raw (approx. 85 %) and FGD gypsum (approx. 15 %) for the cement industry accounted for an estimated 54 000 t. The remaining demand for gypsum of around 380 000 t is covered by mining and production in Switzerland. The domestic production processes are limited to wallboards, plaster, screeds and mortar as well as gypsum for cement production.

The current situation concerning recycling is as follows: There is around 230 000 t of waste gypsum in Switzerland that could be easily recycled.[19] This amount corresponds to approximately 60 % of the Swiss production of gypsum building materials. Currently, only a small portion of this is recycled.[18] This relatively low recycling rate can be explained by the sufficient availability of raw gypsum in Switzerland and its neighbouring countries.

With estimated resource extraction costs of 10–15 CHF / t the conditions for the economically viable recycling of gypsum are not favourable (Tab. 2). In addition, the locally recycled gypsum competes with the FGD gypsum supplies from abroad. However, the largest quantities come from the brown coal power plants in eastern Germany, for which the transport costs of an export to Switzerland are likely to be too high. Thus, the competition with FGD gypsum is limited to power plants in the closer neighbouring countries.

Table 2: Rough estimate of the processing costs of gypsum waste. Material value / savings: neg, costs: pos.

Material	Share [%]	Target process	Costs [CHF / t]	Costs [CHF]
Gypsum part	80	Production of gypsum	-10.00	-8.00
Cardboard part	8	Combustion in MSWI	120.00	9.60
Additives part	12	Production of gypsum	-10.00	-1.20
Total costs of recycled gypsum			[CHF / t]	0.40
Costs of the construction, operation and maintenance of the plant			[CHF / t]	25.00
Total processing costs			[CHF / t]	25.40

In Switzerland the costs of landfilling gypsum waste are in the range of 50 CHF / t, although there are large regional differences. The costs for recycling gypsum waste from wallboard and plasterboard are only about of 25 CHF / t , which means that if less than 25 CHF / t are spent for sorting and waste collection logisitics, reycling is more favourable than landfill disposal.

For cement production, the costs of the required gypsum are, depending on the location, between 27 and 55 CHF / t , including transportation. If the gypsum recycling plants were operated in the vicinity of the cement plants, the raw material costs of the cement plants could probably be minimised. Therefore a great deal of potential can be seen in the recycling of gypsum from an economic point of view, especially since we can expect significantly increasing gypsum waste streams in the future.