The Elements of Magnetics

Steve Constantinides
Arnold Magnetic Technologies Corporation, 770 Linden Avenue, Rochester, NY 14625, U.S.A.
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ABSTRACT

The 20th century saw rapid and dramatic improvements in permanent magnet materials. It has been 31 years since the discovery of neodymium-iron-boron and numerous companies and laboratories are seeking to produce a new and superior material. Topics discussed herein are material options, economics of selected materials and market drivers in material selection. Market issues include manufacturability by shape, size, and material yield; raw material supply including cost and dependability of the supply chain; raw material and magnet product price stability; development of applications based on commercial needs, government legislation and consumer demand. "Need is the mother of invention" and no discussion would be complete without covering why a new material would be beneficial from an applications point of view especially in energy production and consumption. Therefore, an introduction will be provided for select, major applications using permanent magnets and the growth forecasts for these.

INTRODUCTION

Research in magnetic materials has been conducted for a few hundred years. Permanent magnets have especially benefitted from advances in key magnetic properties. The 20th century saw particularly significant improvements. [(1)] The last substantially improved material has been so superior to any that came before it that it has been widely adopted. This material is neodymium-iron-boron (NdFeB, "Neo"). It was discovered in 1981 by accident at the Naval Research Laboratories during research for an improved soft magnetic material. Three patents were issued for it including process, composition and product patents. The material was then optimized and commercialized by Sumitomo, General Motors and numerous other companies in Europe, the USA and China. The first commercial magnets were sold by Crucible Magnetics of Elizabethtown, Kentucky, in November of 1984.

The first major application for Neo was in hard disk drives. By 1990, it was estimated that 75% of Neo production was for hard disk drives in 1) the sintered magnets used to move the read/write head and 2) for the compression bonded ring magnet in the spindle motor. Other industrial and commercial motors also benefitted from Neo magnets' combination of high magnetic output and relatively low price.

During the 1980s and early 1990s almost all the rare earths used in magnets came from Molycorp's Mtn. Pass California mine. The mine was operated primarily for other rare earths such as europium for color cathode ray tubes and cerium for glass polishing. The magnet rare earths were sold from the residual materials after separation. By the mid 1990's the demand for neodymium exceeded what was extracted in natural ratio causing stockpiling of cerium and lanthanum.[(2)] By the late 1990s China had become a major supplier of rare earths (oxides, metals and alloys) eroding Molycorp's domination of the market.[(3)]

Despite warnings by China as early as 2005 about the coming rare earth material supply problem, corrections to the supply dynamic were to slow-to-develop and by the great recession of 2009, almost 97% of rare earths were coming from China. Rising prices and threats of inadequate supply caused market panic. Thus the great interest in rare earths and in alternatives to rare earths, especially in magnets.

DISCUSSION

The word elements, as presented here, refers first to the fundamental science of magnetism. Understanding the principles of magnetism is necessary for understanding the market and its responses to supply disruption.

The second "element" refers to those market forces that drive utilization of one material versus another and to what extent a material is used at all. We'll examine three markets: vehicular traction drives, wind power generation of electricity, and electronics – especially memory storage devices.

The next element refers to those factors controlling material selection – the economics of materials. A side issue, but one that has been very important with regard to Neo magnets during 2011 is the threat of non-supply, a total cut-off of the magnets or raw materials used to make Neo to companies and consumers outside China.

Then we come to the elements themselves. Which ones have been used in magnetic materials, which elements might be used and what alloys are being investigated, which is the last element of the discussion – research and development – efforts to find the next permanent (or soft) magnet.

Elemental Magnetism

A good place to begin when speaking about magnetism is with the magnetic hysteresis loop. In response to an externally applied field, magnetic materials generate an internal field – an induced field. As we apply a stronger field in one magnetic direction (+H), weaken it and then apply it in the opposite direction (-H) we cause the internal field to respond accordingly. If we plot the applied field (H) versus the induced field (B), we have what is called the hysteresis loop of the magnetic material.[4,5] (Refer to Figure 1).

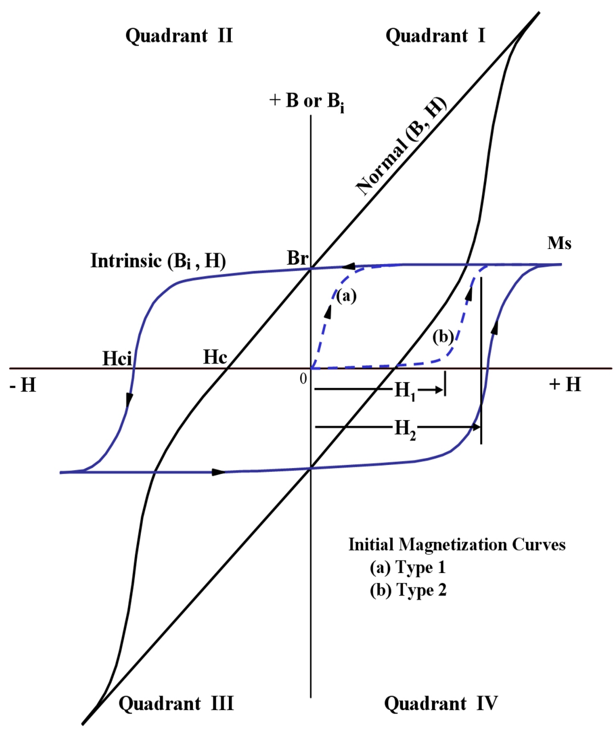


Figure 1. Magnetic hysteresis loop showing the relationship between an applied and induced magnetic field in a ferromagnetic material.[5]

We measure the combination of applied and induced field and represent it as the "Normal Hysteresis Loop". When we subtract the magnitude of the applied field from the combined field, the result is the "Intrinsic Hysteresis Loop". As we cycle the magnet around the hysteresis loop (by changing the applied field), we see that the 1st and 3rd quadrant are identical, though of reverse sign just as the 2nd and 4th quadrants are identical but of reverse sign.

Over time, several variations have been used for the terms representing magnetic characteristics. For example, Hc is also called H_{cB}, Hci is H_{cJ}, BHmax is $(BH)_{max}$ and Ms is the same as J_S. One reason for continuation of the older terms is avoidance of subscripts in routine typing. The combination of SI and CGS terminology, old and new abbreviations, and points on the Normal and Intrinsic loops can be daunting.

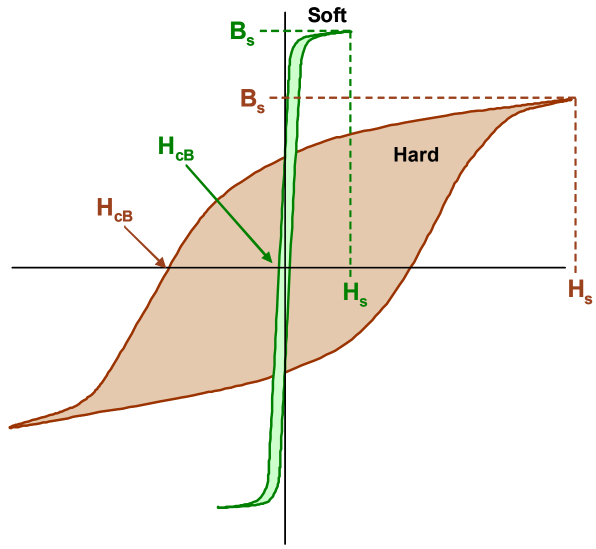


Figure 2. Comparison of soft and permanent magnet hysteresis loop shapes. The value of H_{cB} for permanent magnets is much larger than for soft magnetic materials.

The magnetic hysteresis loop provides a great deal of information about the material.
First, it identifies the type of magnet: soft or permanent. A magnetically "soft" material has very small H_{cB} and the area within the loop is small. On the other hand, a permanent magnet exhibits a much greater H_{cB} and a larger area within the loop. Both curves, as shown in Figure 2, are Normal curves. The curve with higher induction is a soft magnetic material typical of silicon iron (Si-Fe) and the curve with higher H_{cB} is typical of alnico 8. The values of B_s represent the magnetic saturation and H_s is the applied field strength at which saturation occurs.

The energy to force a magnet around the loop is proportional to the area within the loop. Therefore, transformers and laminations in motors benefit from being made of magnetically soft materials with very low H_{cB} and correspondingly small areas within the loop.

There is actually a continuum of materials from very soft to very hard. We can divide them into soft and hard magnetic materials as is commonly done or we can split them into three categories (as shown in Table I) wherein each of the three categories has specific benefits for select applications. For example, semi-hard materials are often used in hysteresis-coupled drives. For convenience we have assigned arbitrary values of H_{cB} to distinguish one category from the next, but there is no hard rule regarding the differentiation in category. Note that alnico is considered (for the most part) a permanent magnet material. Yet the Normal curve is used to describe its magnetic properties, not the Intrinsic curve because early grades of alnico with small H_{cB} exhibited values of H_{cJ} that were only slightly higher. Other materials, such as FeCrCo, can have various levels of H_{cB} by adjusting the final heat treatment time, temperature and quench rate.

When Ferrite magnets were invented in the mid 1950's, suddenly we had a material with H_{cJ} much larger than H_{cB} and it became common practice to provide both the Normal and the Intrinsic curves in product literature. This continued, of course with SmCo, Neo and SmFeN magnets.

A list of the key characteristics of commercial soft magnetic materials includes:

- Saturation magnetization (B_s, J_s or M_s)

		H_{cB}	H_{cJ}	H at Bsat	Bsat. (~Msat.)[A]
Overview	Soft	< 25	< 25	< 700	
	Semi-Hard	25 to ~700	25 to ~700	~700 to 2000	
	Permanent	> 700	> 700	> 2000	
Soft	Supermalloy	0.003		2	7,800
	Deltamax	0.08		10	16,000
	Si-Fe	0.6		100	19,500
Semi-Hard	FeCrCo[B]	50-300		700	9,000 - 12,000
	Remalloy	250		1,000	15,200
	Vicalloy	250		1,000	14,500
	Cunife	500		1,500	8,400
	Cunico	700		1,500	8,800
Permanent	Alnico 5-7	740	750	2,000	13,500
	Alnico 8	1,600	1,800	4,500	10,500
	Ferrite (Ceramic 8)	3,000	3,500	6,000	4,500
	SmCo 1:5 (R20)	8,700	30,000	30,000	10,000
	SmCo 2:17 (R26)	9,900	25,000	45,000	11,500
	NdFeB (N38SH)	12,000	20,000	35,000	14,000

[A] Soft and Semi-Hard materials use Bsat.; PM materials use Msat.
[B] FeCrCo can be heat treated to yield many combinations of Hc and Bsat.

Table I. Categorization of magnets as soft, semi-hard or permanent magnets. The division between categories is approximate. This is a partial listing of products showing examples of each category.

- Coercivity (H_{cB}) (smaller is better)
- Ease of magnetization (maximum permeability is large)
- Electrical resistivity (higher is better)
- Usable temperature range
- Small magnetization change with temperature (RTC)
- Corrosion resistance
- Compromise of physical strength and malleability
- Formability, for example to make laminations
- Manufacturability and formability
- Material availability and product cost

The top four characteristics have a dominant affect upon eddy current and hysteresis loss of the material, both of which cause the material to absorb energy and heat up. In addition to energy loss, heating usually worsens physical and magnetic quality. Many magnetically soft materials are also physically "soft". That is, they are malleable – can be rolled to thin strips, bent to shapes or easily machined. If the material is deformed or mechanically worked, it may be necessary to anneal it to remove strain and re-establish low H_{cB}.

Magnetic properties of interest for soft magnetic materials lie either in the entire hysteresis loop or in the 1st quadrant. The two most interesting values in the 1st quadrant are the maximum permeability which is the slope of a line from the origin to the "knee" of the curve, such as the dashed line in this chart (Figure 3) touching the Supermendur curve at the circular mark. The higher the slope, the easier the material is to magnetize. The second figure of interest is the saturation magnetization – on these curves, the value of B_s, and shown here for Deltamax.

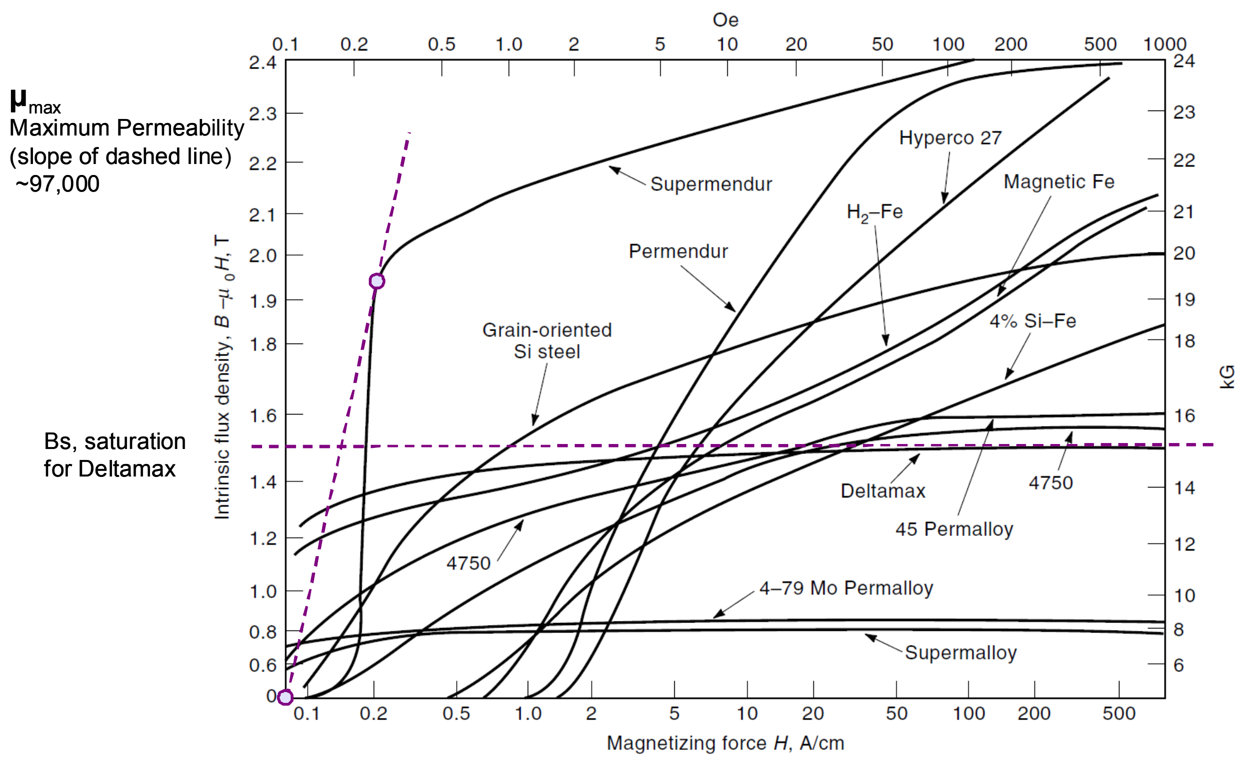


Figure 3. Soft magnetic alloys' 1st quadrant hysteresis information[4] with an example of maximum permeability indicated for Supermendur and Saturation magnetization indicated for Deltamax.

Permanent magnets have a slightly different list of key characteristics.

- Flux density (Br)
- (Maximum) Energy Product (BHmax)
- Resistance to demagnetization (HcJ)
- Usable temperature range
- Magnetization change with temperature (RTC)
- Demagnetization (2nd quadrant) curve shape
- Recoil permeability
- Corrosion resistance
- Physical strength
- Electrical resistivity
- Magnetizing field requirement
- Available sizes, shapes, and manufacturability
- Material availability and product cost

For each application a subset of these characteristics will determine how well a material is suited to the application. The most discussed figure of merit is "maximum energy product", abbreviated BHmax (or $(BH)_{max}$). The amount of energy we can temporarily store in a magnetic circuit is proportional to a magnet's maximum energy product. Also important, since these are supposed to be "permanent" magnets and we would not want them to demagnetize, is the value of H_{cJ}, a measure of resistance to demagnetization – the greater the value of H_{cJ}, the more resistant to demagnetization.

Magnetic properties change with temperature. When selecting a material for an application it is important to know what the properties are over the entire range of expected temperatures. Changes in flux output as a function of temperature can be calculated using the Reversible Temperature Coefficient of Induction (RTC). For example, changes in resistance to demagnetization, HcJ, are calculated using the Reversible Temperature Coefficient of (Intrinsic) Coercivity.

For permanent magnets, we are primarily interested in the 2nd quadrant of the hysteresis loop. Figure 4 is typical of the "demag" curves presented in product literature for ferrite, SmCo and Neo magnets. The key figures of merit for permanent magnet materials are indicated on this chart. The maximum energy

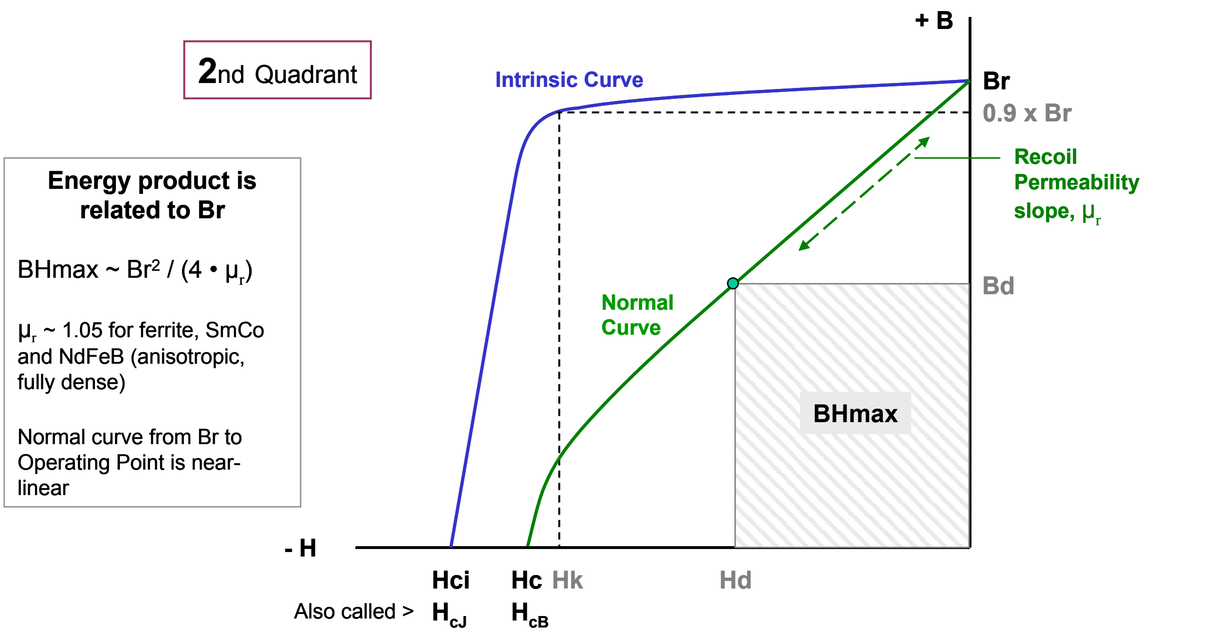


Figure 4. 2nd quadrant of the hysteresis loop for permanent magnets – typical of ferrite, SmCo and Neo magnets. Key magnetic parameters are indicated.

product (BHmax) can be estimated from just the B_r as shown in the equation in Figure 4 – assuming an appropriate value for recoil permeability. Conversely, the Br can be estimated when the maximum energy product is known. These calculations can only be made with a "straight line" material. As shown here, this material would be considered a "straight line" (Normal curve) or "square loop" (Intrinsic curve) material since the Normal curve is straight (at least to the maximum energy point).

The following four commercially available magnet materials represent over 95% of permanent magnet sales: 1) Alnico, 2) Ferrite, 3) SmCo (1:5 and 2:17) and 4) Neo. Each has advantages that make it more suitable for a specific application. Therefore, even Alnico, commercialized in 1932, is still utilized. The values shown in Table II represent a practical range of available properties for each material. A satisfactory new material will have a propitious combination of these values as indicated in the rightmost column.

Table II. Values for the key characteristics of commercially available permanent magnets. The right column provides indicators of what would be a better magnet material.

Characteristic	Units	Alnico 5-7	Alnico 8	Ferrite 8	Ferrite 9	SmCo 1:5	SmCo 2:17	NdFeB 33EH	NdFeB 48M	Indicator
Flux density (Br)	Tesla	1.35	0.85	0.39	0.45	0.9	1.1	1.15	1.39	> is better
Energy Product (BHmax)	kJ/m^3	60	46	28	37	175	230	230	370	> is better
Resistance to demagnetization (Hcj)	kA/m	59	125	245	370	2400	1600	2400	1115	> is better
Usable temperature range	°C	4 K to 520 ºC	4 K to 520 ºC	-40 to 150 ºC	-40 to 150 ºC	4 K to 520 ºC	4 K to 520 ºC	150 K to 200 ºC	150 K to 100 ºC	minimum -40 to 200 ºC
Induction change with temperature (RTCof Br)	%/ºC	-0.02	-0.01	-0.2	-0.18	-0.045	-0.035	-0.11	-0.12	< is better
2nd quadrant Normal curve shape		Curved	Curved	Straight	Straight	Straight	Straight	Straight	Straight	Straight
Recoil permeability	B / H	2	2	1.04	1.04	1.03	1.05	1.04	1.05	~1
Corrosion resistance		Excellent	Excellent	Outstanding	Outstanding	Good	Good	Fair	Fair	Outstanding
Physical strength	MPa	55	205	65	70	120	120	285	285	> 50 also "tough"
Electrical resistivity	□π • cm	47	50	10^6	10^6	55	90	180	180	> is better
Magnetizing field requirement	kA/m	120	240	480	800	2000	4000	2700	2700	Less than 4000
Coefficient of Termal Expansion	$\%/ ^{\circ}C \times 10^{-6}$	11.5	11	10 to 15	10 to 15	7 to 14	11 to 13	7.5 to -0.1	7.5 to -0.1	< 15
Approx Current Price (ballpark estimates)	$/kg	$40	$35	$8	$15	$120	$100	$200	$150	< is better
Relative Cost at 20 ºC	$/MGOe	$5.3	$6.1	$2.3	$3.2	$5.5	$3.5	$6.9	$3.2	< is better
Relative Cost at 200 °C	$/MGOe	$5.7	$6.3	$5.6	$7.1	$6.5	$3.9	$10.8	n/a	< is better

Elements driving growth of the magnet market

Since 2010, major topics of interest within the magnet and user industries have been pricing and availability of rare earths and rare earth magnets. The materials shown in Table III comprise the family of Rare Earth magnets.

SmCo has been discussed as a replacement for Neo magnets. Although SmCo magnets are superior for elevated temperature applications, the raw materials

Table III. The four commercially available rare earth magnets

4%
- $SmCo_5$
  - Sintered (powder metallurgy)
- Sm_2Co_{17} – actually $Sm_2(CoFeCuZr)_{17}$

95%
- Neo (neodymium iron boron)
  - Powder for bonded magnets: compression, extruded, injection molded
  - Sintered (powder metallurgy)
  - Hot rolled (no longer made): modified composition; Seiko-Epson
  - Die-upset / forged, fully dense: Magnequench MQ-3 process (original and modified); Daido Electronics

1%
- SmFeN
  - Powder metallurgy process resulting in a fine powder suitable for bonded magnets
  - Unstable above ~450 °C – no known method for achieving a fully dense magnet

Percent by weight of commercially produced rare earth magnets used in Neo magnets are more generally available and at historically lower cost. This has propelled Neo magnets into a dominant position. However, for Neo to perform successfully at elevated temperature requires substituting a heavy rare earth, especially dysprosium, for up to 1/3 of the neodymium (up to ~11 weight percent of a magnet). (Heavy rare earths other than dysprosium are even more rare). In years 2011 and 2012, the supply of dysprosium has been inadequate, resulting in high material prices. There is likely to be a continuing long-term shortage as no significant new supplies have been identified.

SmFeN decomposes at a fairly low temperature, starting at ~450 °C, preventing consolidation to full density. Because it must be used as a (low-temperature-formable) bonded magnet, maximum energy product is limited by dilution with a non-magnetic binder. This has developed as a niche product.

Where are rare earth magnets used? Table IV is a break down of applications for rare earth magnets with approximate percentages going into each category. It represents about 80% of the market for rare earth magnets. Much information regarding the other 20% is in domestic markets in China, India and other countries where definitive information has not been available.

Table IV. Applications for rare earth magnets with approximate fraction of all applications and estimates of requirements for neodymium and for dysprosium.[6]

	2010				**2015**			
	yr 2010	**Magnet**	Oxide, tons		yr 2015	**Magnet**	Oxide, tons	
Applications	**% of mix**	tons	**Nd**	**Dy**	**% of mix**	tons	**Nd**	**Dy**
Motors, industrial, general auto, etc	25.5%	15,871	7,122	1,059	25.0%	24,316	10,912	1,622
HDD, CD, DVD	13.1%	**8,140**	4,196	0	14.4%	**14,040**	7,237	0
Electric Bicycles	9.1%	**5,680**	2,549	379	8.2%	**7,955**	3,570	531
Transducers, Loudspeakers	8.5%	5,290	2,727	0	6.5%	6,322	3,259	0
Unidentified and All Other	6.5%	4,046	1,995	90	6.0%	5,836	2,878	130
Magnetic Separation	5.0%	3,112	1,466	138	3.4%	3,307	1,558	147
MRI	4.0%	2,490	1,228	55	1.5%	1,459	720	32
Torque-coupled drives	4.0%	2,490	1,117	166	2.5%	2,432	1,091	162
Sensors	3.2%	1,992	982	44	1.5%	1,459	720	32
Hysteresis Clutch	3.0%	1,867	879	83	1.5%	1,459	687	65
Generators	3.0%	1,867	769	194	1.0%	973	400	101
Energy Storage Systems	2.4%	1,494	670	100	2.5%	2,432	1,091	162
Wind Power Generators	2.1%	**1,300**	583	87	10.1%	**9,810**	4,402	654
Air conditioning compressors and fans	2.0%	1,245	559	83	2.5%	2,432	1,091	162
Hybrid & Electric Traction Drive	0.9%	**570**	214	80	6.3%	**6,160**	2,308	867
Misc: gauges, brakes, relays & switches, pipe inspection, levitated transportation, reprographics, refrigeration, etc.	7.7%	4,792	2,186	285	7.1%	6,906	3,113	447
Total	100.0%	**62,246**	29,243	2,843	100.0%	**97,296**	45,037	5,115

Nd: 54% increase
Dy: 80% increase

REO requirement includes 80% oxide to metal, 97% metal alloying, and 80% magnet manufacturing material yields.

There are significant geographic differences in product mix depending on location of manufacture and what market segment is being served. China now manufactures about 80% of all rare earth magnets, Japan makes 17%, and about 3% are made in Europe and the USA. Chinese companies have more recently been moving aggressively into the value added (downstream) markets.

Because of raw material supply price variability and questions about availability, numerous magnet-using companies have changed product plans: product roll-outs have been delayed, new designs are being re-evaluated to use alternate magnet materials and technologies without permanent magnets are being investigated and utilized.

The change in magnet usage between 2010 and 2015 suggests a need for an increase in supply of neodymium (oxide and metal) of about 54% while dysprosium requirements will be 80% higher. Without adequate dysprosium, neo magnet growth will lag. To understand the market dynamics better, let's look at a few specific applications – those in bold face in Table VI.

Cars and small trucks are increasingly being driven by some combination of electric motor (traction drive motor) with or without an internal combustion engine (ICE). Forecast sales in the USA for 2012 of cars and small trucks using alternate drive systems, based on sales through August, are 461,250 units.[22] 2011 and 2012 represent watershed years in that EV (electric vehicle) and PHEV (plug-in hybrid electric vehicle) sales have just started. Change in consumer preferences are due primarily to the high price of gasoline[21], overall improvement in economic prosperity, market acceptance of alternate drive systems and the increasing number of models to appeal to a wider consumer audience.

Alternate drive vehicle sales as a percentage of overall sales in the USA is increasing. Based on sales through August, 2012 may end with these being over 3.1% of sales despite the smaller-than-forecast number of models available in 2012 – 54 versus JD Power's forecast of 103.[20] There should be no doubt that we are at a major turning point regarding use of hybrid and full electric vehicles.

A second developing market for permanent magnets is wind power – both generation of commercial electricity by large, tower-mounted generators and smaller systems for home and business installations. In 2008, DOE forecast installations of commercial electric wind power generation[7] per the plum-colored bars on Figure 5. I have plotted blue bars to show actual installations each year (through 2011). Actual installations have exceeded forecast largely due to government incentives. Future installations will depend upon continuing incentives in combination with higher alternate fuel and conventional power production costs.

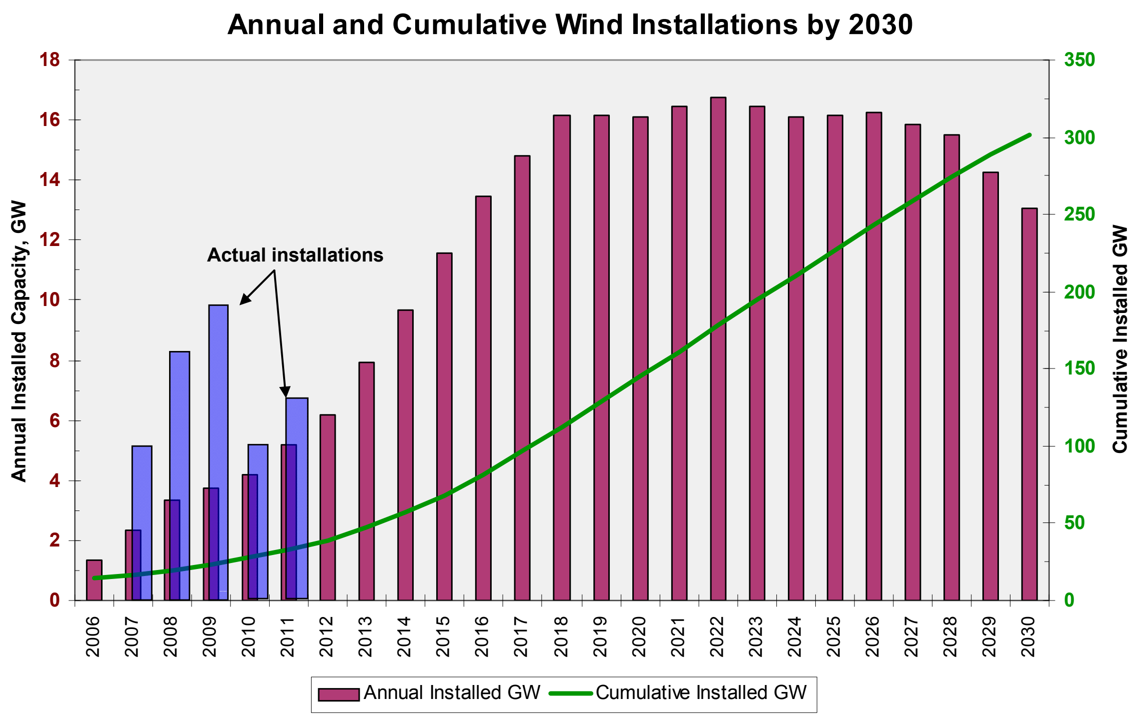
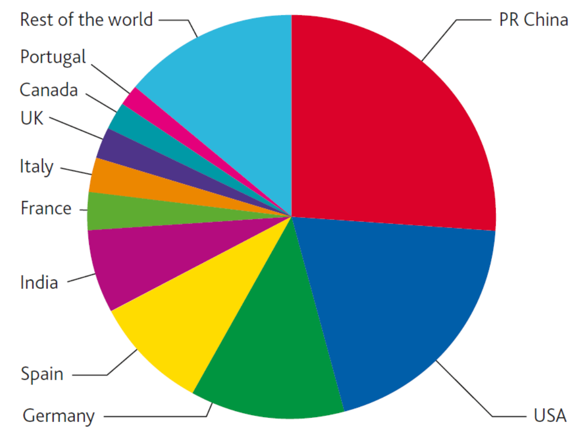


Figure 5. AWEA forecast for commercial wind power installations through 2030 with actual installations indicated through year 2011[7]

Countries outside the USA have also been installing wind power with China leading the surge, installing 43% of new wind power in 2011.[8] (See Figure 6). Prior to 2005, China's wind power industry was close to non-existent. Since then it has grown rapidly and now cumulatively China has more wind power generation installed than any other country (26.2% of global generation).

Consensus estimates of the fraction which are permanent magnet (PM) type generators recently installed are 5% in the US and Europe and 25% in China. These numbers are highly speculative as producers are reluctant to make public information about generator type. Reasonable estimates for

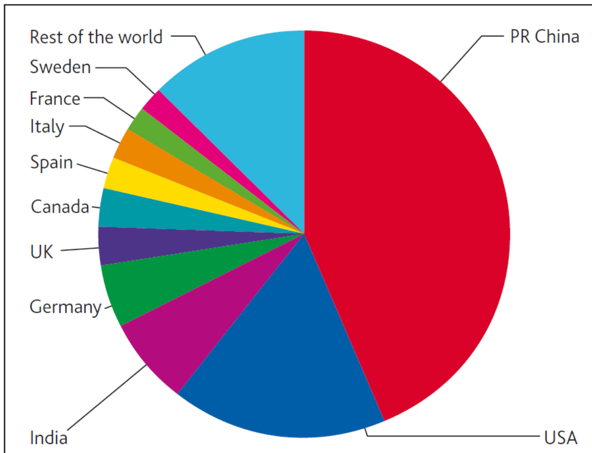
Top 10 cumulative capacity Dec 2011



Country	MW	% SHARE
PR China	62,364	26.2
USA	46,919	19.7
Germany	29,060	12.2
Spain	21,674	9.1
India	16,084	6.8
France**	6,800	2.9
Italy	6,737	2.8
UK	6,540	2.7
Canada	5,265	2.2
Portugal	4,083	1.7
Rest of the world	32,143	13.5
Total TOP 10	205,526	86.5
World Total	**237,669**	**100.0**

** *Provisional Figure* *Source: GWEC*

Top 10 new installed capacity Jan-Dec 2011



Country	MW	% SHARE
PR China	17,631	43
USA	6,810	17
India	3,019	7
Germany	2,086	5
UK	1,293	3.2
Canada	1,267	3.1
Spain	1,050	2.6
Italy	950	2.3
France**	830	2.0
Sweden	763	1.9
Rest of the world	4,865	12.0
Total TOP 10	35,699	88
World Total	**40,564**	**100.0**

** *Provisional Figure* *Source: GWEC*

Figure 6. Global wind power installations[8]

kilograms of Neo required per megawatt are 600 kg/MW in direct drive and 200 kg/MW in hybrid drive generators.

Germany has announced that they will shutter nuclear power plants by 2022[9,10] and depend more on renewable resources. Nuclear power in Germany accounted for 17.7% of national electricity supply in 2011, down from 22.4% in 2010.[9] But wind is an unpredictable power source and can only be a small fraction of overall generating capacity; estimates are ~20%.

The wind power generating market is going through a shakeout that will likely last well into 2013 or until a more clear picture of the following issues is available: magnet pricing and availability, government subsidies, alternate fuel pricing (natural gas, oil, coal), strategies regarding continued or increased use of nuclear power, etc. In the longer term, superconducting wind power generation may be used on wind towers generating 5 or more MW (megawatts), however commercial installations are not expected for at least ten years as designs are developed and tested and engineering problems addressed and overcome.

One of the continuing, main uses for Neo rare earth magnets is in hard disk drives (HDDs), CDs and DVDs where a bonded Neo magnet is used for driving the spindle motor and sintered magnets are used for positioning the read/write head and providing a clamping force (in some CDs and DVDs). Even though the amount used per drive is small, 6 to 13 grams, the huge quantity of devices requires large amounts of rare earth magnets. Importantly, these devices use no dysprosium. In Figure 7 we see continuing growth of the HDD market despite the surge in SSD (solid state drives, thumb drives).

Requirements are increasing for individual and commercial storage of pictures, music, server farms for cloud computing, file back-up, etc. HDDs are commonly 1 to 2 or more terabytes in size while the larger SSD devices boast 128 GB. So while SSD eats away at the lower end of storage requirements, especially in portable devices, HDDs continue to grow in usage for higher volume storage.

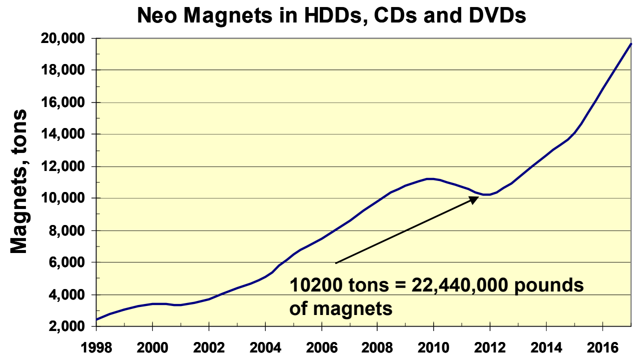


Figure 7. Consumption of Neo magnets in HDDs, CDs and DVDs(19)

Economic Elements

An examination of product selling price of each of the four major commercial permanent magnets highlights the high cost of rare earth magnets – primarily due to the cost of the raw materials. Many factors such as shape complexity, size and country of origin contribute to a magnet's manufacturing and selling price. The values shown in Figure 8 are fair estimates for simple shapes and intermediate sizes. Selling price is that observed in the USA and Europe and provides comparative values.

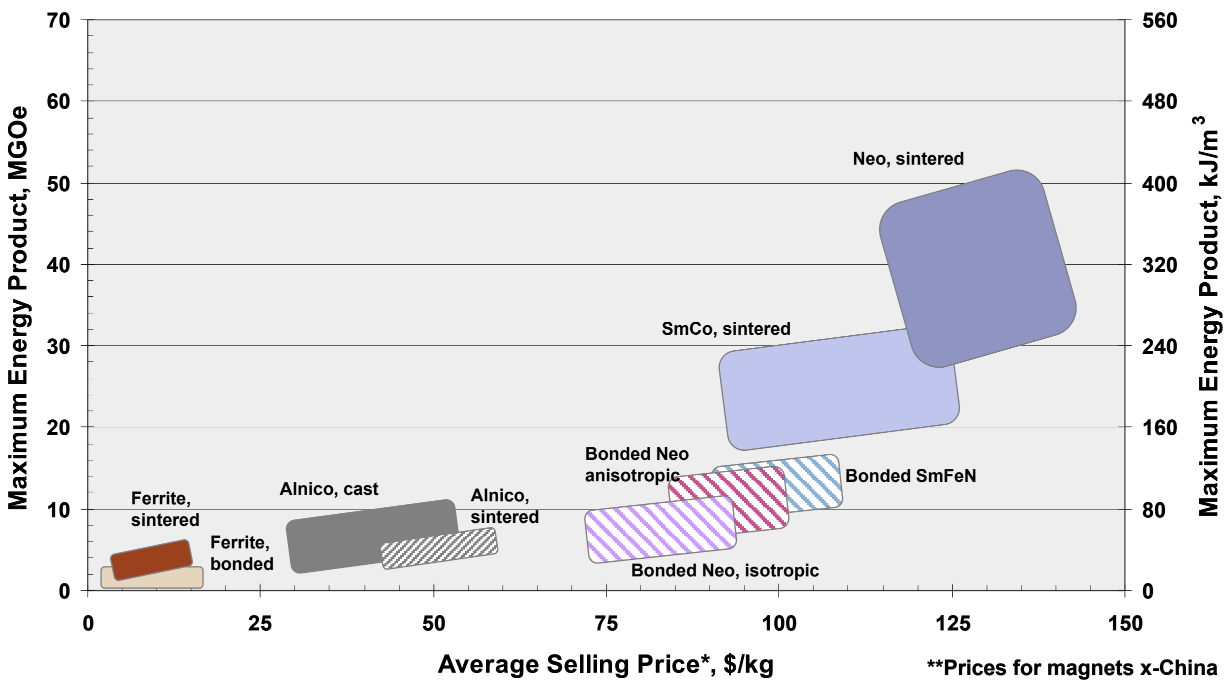


Figure 8. Relative pricing of the most common commercially available permanent magnets. Values represent pricing as of October 2012.

Rare earth materials have experienced price inflation and market disruption (Figure 9). When prices became too high, users of rare earth magnets switched to alternate designs or technologies and are now slow to return. Reduction in demand is helping to speed a continuing drop in material prices. Another way to look at the pricing data is on a normalized basis. Examining them in this way shows, for prices outside of China, a 48-fold increase in price of dysprosium metal between mid 2001 and mid 2011. Other rare earths experienced similar, albeit less severe increases.

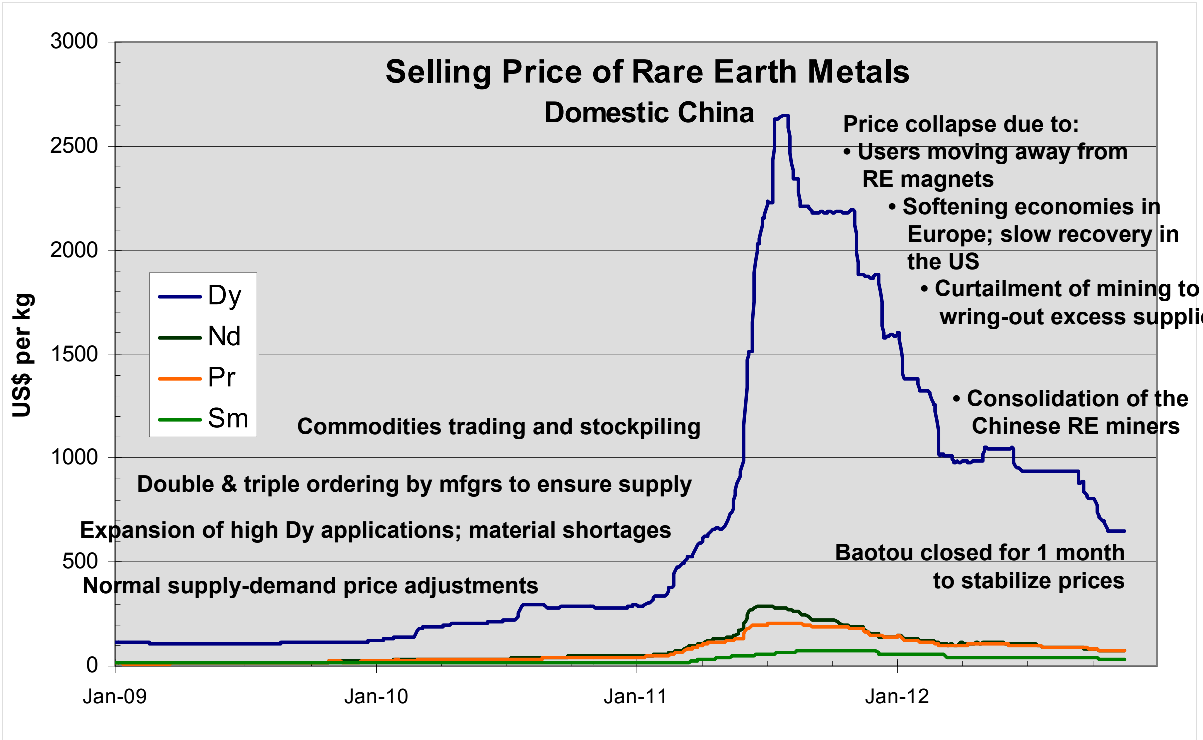


Figure 9. Prices of selected rare earths used in permanent magnets as reported by Asian Metals and Metal Pages with comments by the author regarding causes for the observed changes

While prices of rare earths are coming back down, they will probably not reach levels seen at the low point in 2003. For example, a slow continuing increase is expected in SmCo magnet prices. A stabilization of Neo magnet pricing at higher prices than SmCo is expected due primarily to a combination of high demand and continued high pricing of dysprosium. (Refer to Figure 10). Of course, prices can always change due to government policies, raw material discoveries, new magnetic material invention, changes in market needs, consumer sentiment, etc.

The Elements

Any discussion of commercial viability has to start with the premise that the raw materials are readily available and at a reasonable cost. As a primary ingredient, it's highly recommended to select more common materials such as those above the upper dashed line in Figure 11. Minor ingredients may be from between the upper and lower lines. But elements from below the lower dashed line should be avoided except in the very smallest additions.

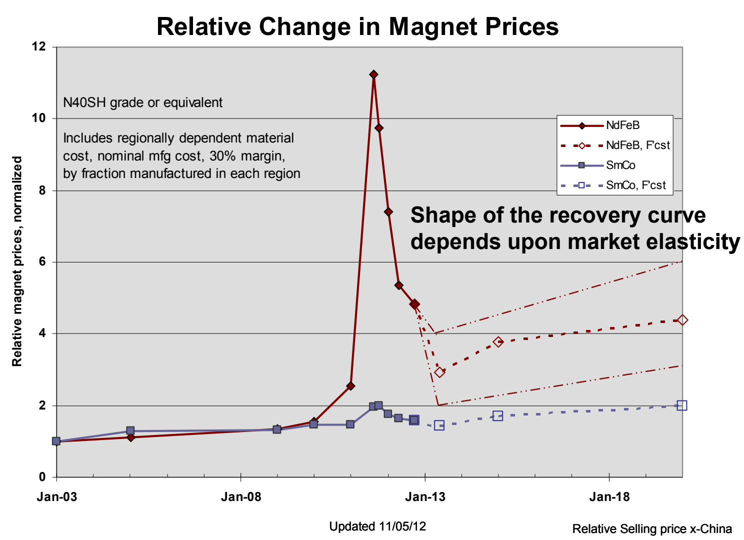


Figure 10. SmCo and Neo relative magnet pricing

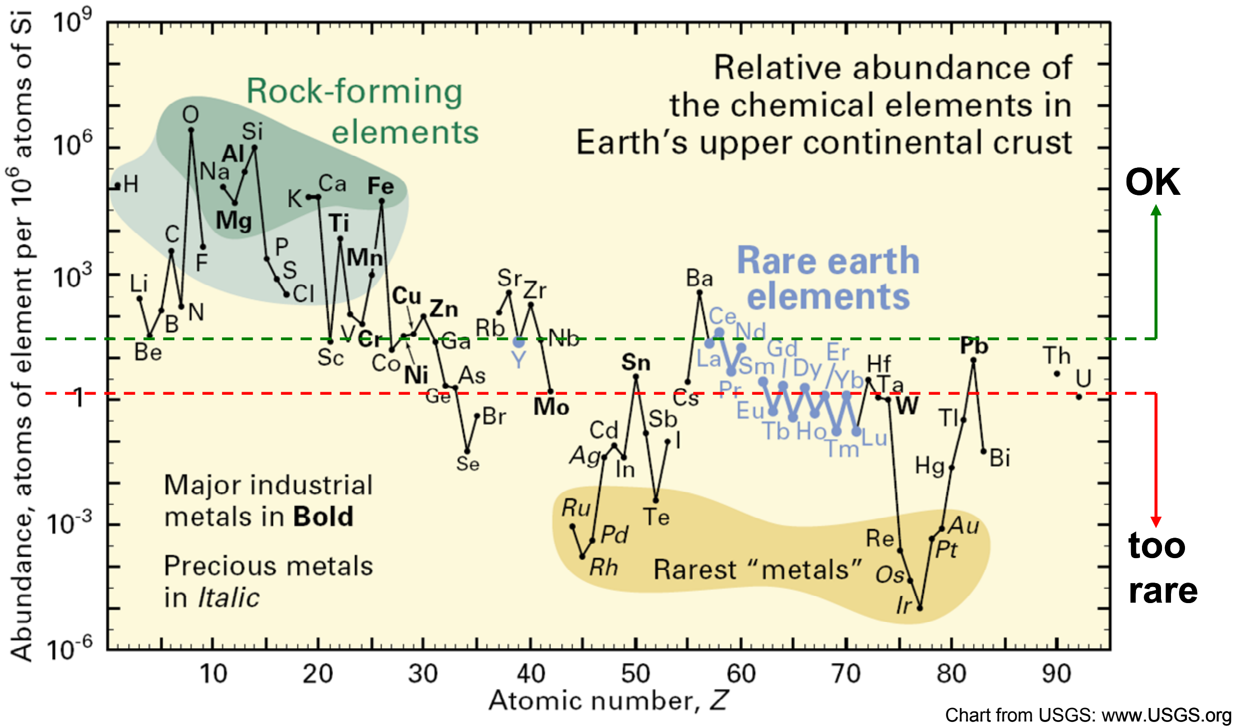


Figure 11. Relative availability of the elements referenced to silicon, the most abundant element[11]

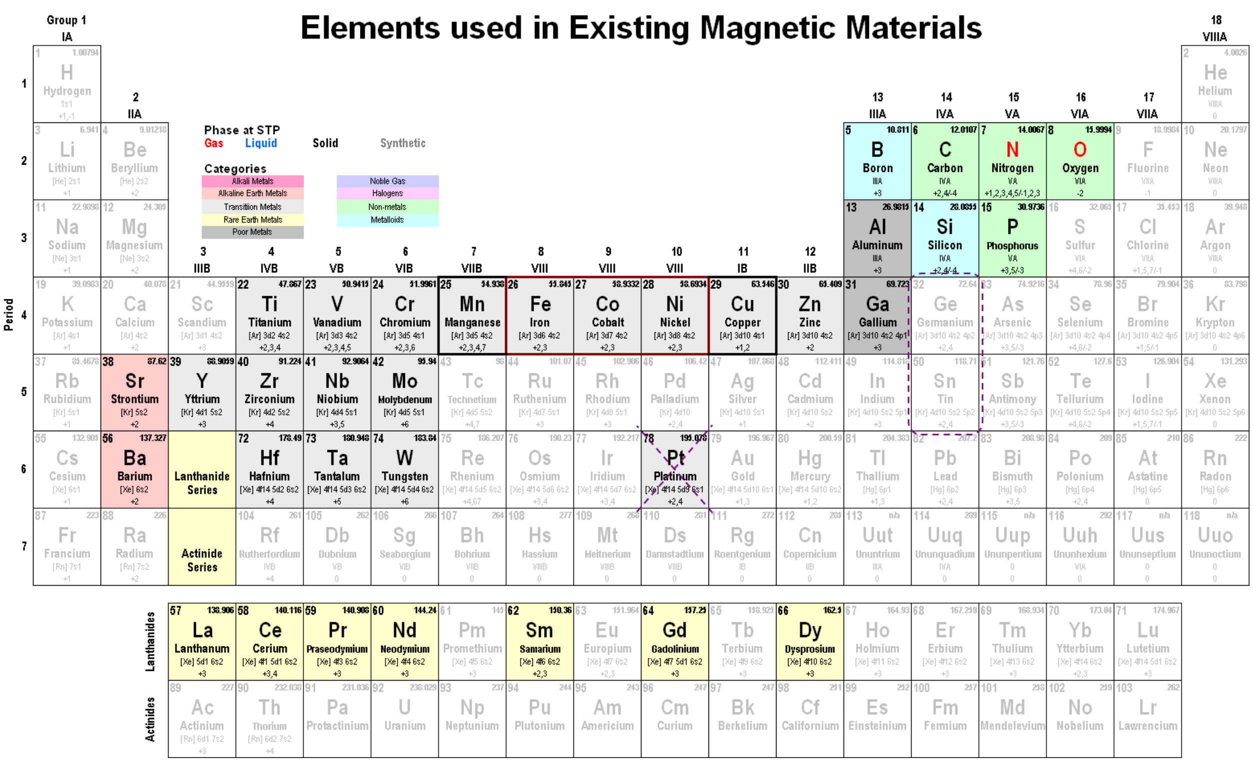


Figure 12. Periodic Table of the Elements with only those elements highlighted that have been and most suitable for making permanent magnets. This conforms to the residual elements after removing those that are (likely) not suitable for magnetics

Let's work with the periodic table to see what elements are likely candidates for use in magnetic materials. I will use a method similar to that of Bill McCallum of Ames Laboratory who kindly shared his notes with me in 2011. (I take personal responsibility for anything presented here).

Let's start thinning the list of elements to remove synthetic (man-made) elements, radioactive elements, noble gases – the inert elements, toxic materials, and let's get rid of the elements that are truly rare such as platinum, palladium, gold, silver, etc. Let's also remove the rock-forming elements and hydrogen. So we're down from 90 naturally occurring elements to 36 – still a large number to research – shown in Figure 12. (Periodic table of the elements is based on an Excel Workbook provided by Vertex.com).

So let's ask a question: what elements have been used over the last 150 years to make magnetic materials? This list, Table V, contains most common magnetic materials and the elements contained in them.

Table V. Permanent magnet materials and the common constituents of those materials

	Major constituents						Minor constituents				Comments
Soft Magnetic Materials											
Iron	Fe										Low carbon mild steel
Silicon Steel	Fe						Si				Si at 2.5 to 6%
Nickel-Iron	Fe	Ni									Ni at 35 to 85%
Moly Permalloy	Ni	Fe					Mo				Ni at 79%, Mo at 4%, bal. Fe
Iron-Cobalt	Fe	Co					V				23 to 52% Co
Soft Ferrite	Fe	Mn	Ni	Zn			O				
Metallic Glasses	Fe	Co	Ni				B	Si	P		Amorphous and nanocrystalline
Permanent Magnets											
Co-Steels	Fe	Co									
Alnico	Fe	Ni	Co	Al	Cu		Ti	Si			
Platinum Cobalt	Pt	Co									
Hard Ferrites	Fe	Sr									Oxygen dilutes; Ba no longer used
SmCo	Co	Sm	(Gd)	Fe	Cu	Zr					
Neodymium-iron-boron	Fe	Nd	Dy	(Y)	B	Co	Cu	Ga	Al	Nb	
Cerium-iron-boron	Fe	Nd	Ce	B							Limited use in bonded magnets
SmFeN	Fe	Sm	N								Nitrogen is interstitial; stability issue
MnBi	Mn	Bi									Never commercialized
MnAl(C)	Mn	Al					C				Not successfully commercialized

If we create a periodic table with these elements highlighted, it is the same as the distilled table above (Figure 12) with these marked exceptions:

1) Platinum: although platinum is rare, platinum-cobalt was the first high performance magnet. It was used to make watch drive motor magnets whose very small size compensated for the high material cost. It is still made but in limited quantities.

2) Germanium and Tin have not been used, at least to my knowledge, in commercial magnets except as very minor additives. Like aluminum and gallium, they might make suitable modifying constituents to assist sintering or phase formation.

As a side note, examination of Figure 11 reveals that copper is no more plentiful than several other sensitive elements including cobalt and about as plentiful as neodymium. Copper is used in motors and generators, even those without permanent magnets. Will copper become an energy critical material (ECE) – in short supply?

<u>Elements in Research</u>

I've split existing research projects into two categories. The first could be called "Variation on a Theme" as it represents an extension of research on materials that have been previously examined. A listing of the materials researched includes:

- SmCo plus exchange-coupled soft phase
- NdFeB plus exchange-coupled soft phase
- Fe-N (variation of SmFeN, interstitial N)
- Mn alloys: MnBi, MnAl(C)
- Heusler alloys
- Alnico – modified to enhance coercivity
- Carbides: FeC, CoC, Co,TM-C,Si
- Modified Ferrites (chemical or structural modifications): La-Co Ferrites, Core-Shell structure ferrites
- Ce-Co,Fe and Ce-Fe,Co-B,C

Although some excellent research and development took place on these materials over extended periods several differences exist between what took place "then" and what is being pursued "now". One difference is that current analytic capabilities are superior to what existed even two or three decades ago either as a new technology or greatly improved one. Secondly, we now have techniques to form these materials with a refined structure at micro- and nano-scales, building bulk structures a few atoms at a time. And we have methods of creating dozens of alloy specimens through co-sputtering techniques greatly speeding up evaluation of promising alloy systems.

Current research is focused on materials that exhibit ferromagnetic properties either naturally or when combined with alloying elements with a focus on the structure. We started our periodic table reduction with 90 naturally occurring elements and ended with 36 promising ones.

The second grouping of projects is what I call the "bottoms-up" approach. It is to take the 36 remaining elements from our experiment with the periodic table and to combine them using computer algorithms to forecast the potential for generating a useful magnetic moment. From the total list of candidates, a short list will be parsed and these most promising alloys produced in the lab and evaluated.

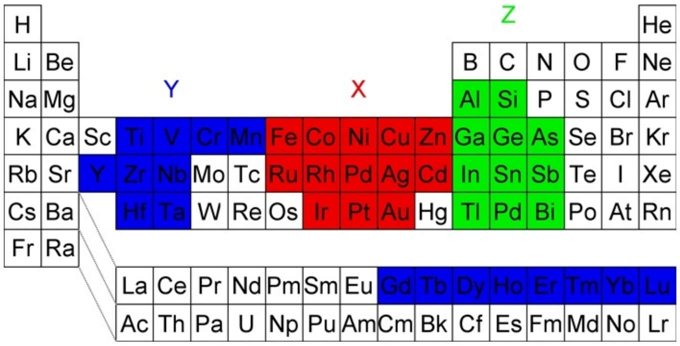
A significant hurdle is to make a nano-particulate material fully dense and to do so in a safe, scalable, and economic manner. A number of compaction/consolidation techniques exist: Hydraulic or mechanical compaction in a die, CIP (cold isostatic pressing), explosive compaction, liquid phase sintering, warm/hot compaction (liquid phase enhanced), hot forging, HIPing (hot isostatic pressing), rolling (with tension), hot extrusion with induced stress/strain, SPS (Spark Plasma Sintering), and friction stir welding. It will be necessary to determine the most successful route to full density.

The beneficial properties of magnetic materials are due in part to either crystal shape anisotropy (e.g. alnico) or magneto-crystalline anisotropy (e.g. ferrite, SmCo and Neo). In either case, during manufacture, the magnetic domains must be mutually aligned to obtain maximum properties. Nano-particulate rare earth magnet alloys have existed for over a decade. However, simultaneous densification and alignment has been a problem awaiting solution.

I've included Figure 13 on Heusler alloys due to their interesting crystalline structure and magnetic anisotropy. They were first identified as a family of materials in 1901 by Friedrich Heusler and have found a recent revival in spintronics.

In addition to the importance of structure in current research is the importance of thermal processing in the development of optimal microstructure and magnetic properties. With the exception of ceramic (hard ferrite) magnets, magnetic alloys are just that – alloys. Therefore, thermal treatments to form a stable and desirable phase structure is common in existing products.

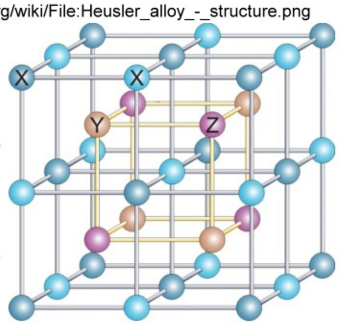
In Figure 14, Karl Strnat shows the development of the hysteresis loop of Sm_2Co_{17} during its thermal treatment. Sm_2Co_{17} is a complex alloy also containing Fe, Cu and Zr. The final heat treatment is required to develop a stable structure which is a combination of the 2:17 phase and a grain boundary phase of SmCo 1:5. (SmCo 1:5 is a simpler composition and structure and does not require a final heat treatment).

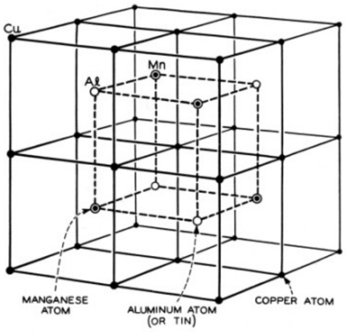


www.riken.jp/lab-www/nanomag/research/heusler_e.html

"A Heusler alloy is a ferromagnetic metal alloy based on a Heusler phase. Heusler phases are intermetallics with particular composition and face-centered cubic crystal structure. They are ferromagnetic—even though the constituting elements are not—as a result of the double-exchange mechanism between neighboring magnetic ions. The latter are usually manganese ions, which sit at the body centers of the cubic structure and carry most of the magnetic moment of the alloy."
Wikipedia

http://en.wikipedia.org/wiki/File:Heusler_alloy_-_structure.png





R.M. Bozorth, *Ferromagnetism*, IEEE Press, p.328

J.M.D. Coey, *Magnetism and Matnetic Materials*, p.394

Table 11.9. Heusler and half-Heusler alloys

	a_0 (pm)	T_C (K)	σ_0 (A m^2 kg^{-1})	m (μ_B)
Cu_2MnIn	621	500	75	4.0
Co_2MnGa	577	694	93	4.1
Co_2MnSi^a	565	985	141	5.0
Co_2MnGe^a	574	905	116	5.1
Co_2MnSn	600	829	97	5.1
Ni_2MnGa	583	380	96	4.2
Ni_2MnSn	605	360	81	4.2
Pd_2MnSb	642	247	63	4.4
$NiMnSb^a$	592	730	93	4.0
$PtMnSb^a$	620	572	60	4.0
Mn_2VAl^a	760	730	59	2.0

[a] Half-metal

Figure 13. Heusler alloys are magnetically ferromagnetic even though the main elements are not. This is an example of how structure can affect the exchange interaction.(13,14,15)

In Figure 15A, the difference in magnetic properties of alnico due to cooling in a magnetic field are quite obvious. Figure 15B shows a typical thermal treatment for alnico to develop these superior magnetics. Alnico is solution treated at high temperature (about 1200 °C) followed by a conditioning treatment effected by controlled cooling from the solution treatment temperature or by isothermal treatment of the magnets. Anisotropic magnets are treated in a magnetic field during spinodal decomposition at ~820 °C. The final 3-stage treatment can be conducted as a 2-stage or slow ramp and is variously called an anneal, a temper or a draw cycle. It requires long thermal treatment times due to the low temperature, causing slow alloy restructuring.

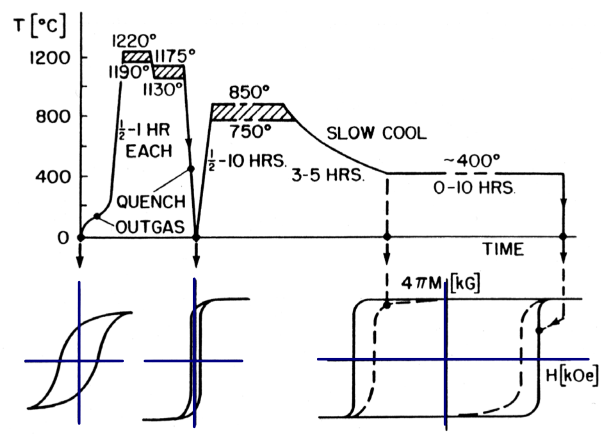


Figure 14. Typical temperature profile for the sintering and heat treating of "2-17"-type $Sm(Co,Fe,Cu,Zr)_{7.2-8.5}$ magnets [16]

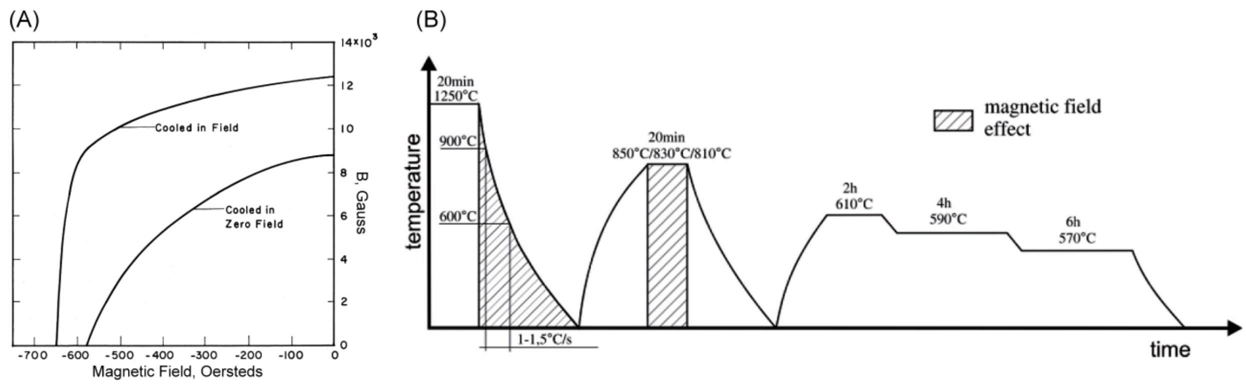


Figure 15. (A) effect of magnetic annealing on alnico 5.(17) (B) Scheme of thermo-magnetic treatment of alnico 8.(18)

We might say that the right composition provides the opportunity for good magnetics and the right thermal treatment creates the right alloy phase structure and optimum magnetic properties.

SUMMARY

Looking once more at the price chart for magnetic materials, Figure 8, research is focused on either improving the properties of less expensive materials or reducing the cost of the high performing materials, all while using readily available raw materials. These new materials will be necessary not as a replacement for but in addition to existing magnetic products. Almost all previously manufactured permanent magnet materials are still in production. New material will likely impact but not eliminate existing materials.

Breadth of acceptance of a new material will depend on many factors not the least of which is manufacturing cost. Ferrite magnets still represent about 85% of all permanent magnets made (on a weight basis) even though they are only 10% of the energy product of Neo magnets. The reasons: low cost and wide availability.

New materials may result from new elemental combinations. But it is more likely that structure and thermal processing will play the major role in new materials' discovery.

ACKNOWLEDGMENTS

William McCallum of Ames Laboratory who first presented the periodic table element review method here and who graciously shared that with me for modification and use here.

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